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Vincent et al.

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(54) **METHODS FOR CONVERTING C2+ OLEFINS TO HIGHER NUMBER OLEFINS USEFUL IN PRODUCING ISOPARAFFINIC KEROSENE COMPOSITIONS**

(58) **Field of Classification Search**
None
See application file for complete search history.

(71) Applicant: **ExxonMobil Technology and Engineering Company**, Annandale, NJ (US)

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(72) Inventors: **Matthew J. Vincent**, Kingwood, TX (US); **Keith H. Kuechler**, Friendswood, TX (US)

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(73) Assignee: **EXXONMOBIL TECHNOLOGY AND ENGINEERING COMPANY**, Spring, TX (US)

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 23 days.

This patent is subject to a terminal disclaimer.

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Primary Examiner — Tam M Nguyen

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(74) *Attorney, Agent, or Firm* — Shook, Hardy & Bacon L.L.P.

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(57) **ABSTRACT**

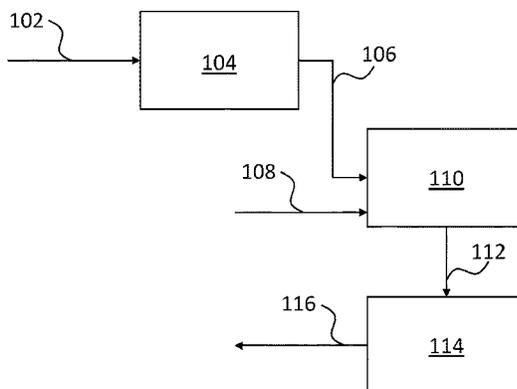
(51) **Int. Cl.**
B01D 3/14 (2006.01)
C07C 1/24 (2006.01)
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A method for producing a blended jet boiling range composition stream may include: oligomerizing an ethylene stream to a C4+ olefin stream in a first olefin oligomerization unit, wherein the C4+ olefin stream contains no greater than 10 wt % of methane, ethylene, and ethane combined; wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen; oligomerizing the C4+ olefin stream and a propylene/C4+ olefin stream in a second oligomerization unit to produce an isoolefinic stream; subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as treat gas to produce an isoparaaffinic stream having no greater than 10 wt

(52) **U.S. Cl.**
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(Continued)

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100 ↘



% olefin content; and using least a portion of the isoparaf-
finic stream to create the blended jet boiling range.

19 Claims, 8 Drawing Sheets

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C07C 2/12 (2006.01)
C07C 5/03 (2006.01)
C07C 7/04 (2006.01)
C07C 7/08 (2006.01)
C10G 69/12 (2006.01)
C10L 1/08 (2006.01)
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 (2013.01); *C07C 7/08* (2013.01); *C10L 1/08*
 (2013.01); *C07C 2529/85* (2013.01); *C07C*
2529/89 (2013.01); *C10G 2300/1092*
 (2013.01); *C10G 2300/301* (2013.01); *C10G*
2400/08 (2013.01); *C10L 2270/04* (2013.01)

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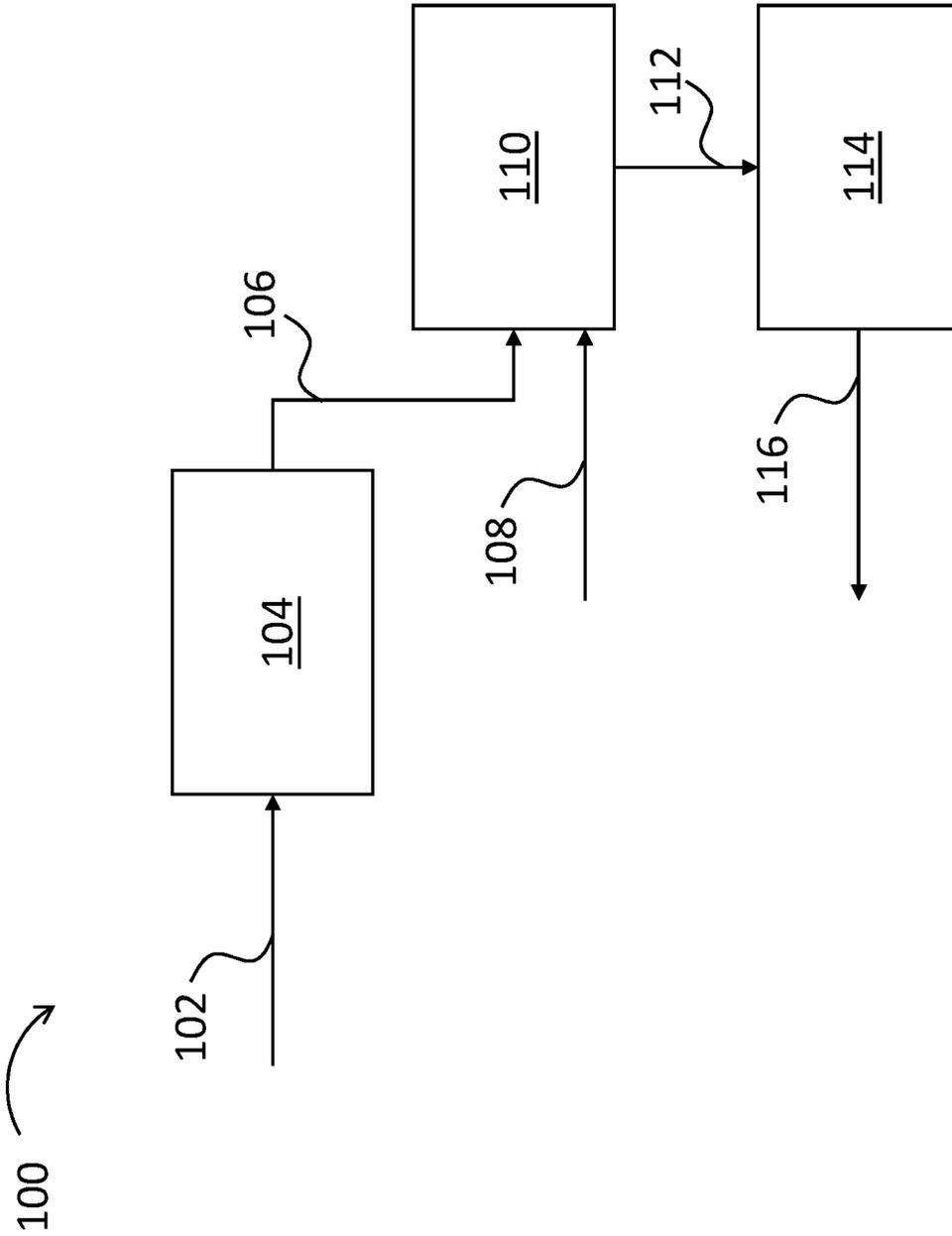


FIG. 1

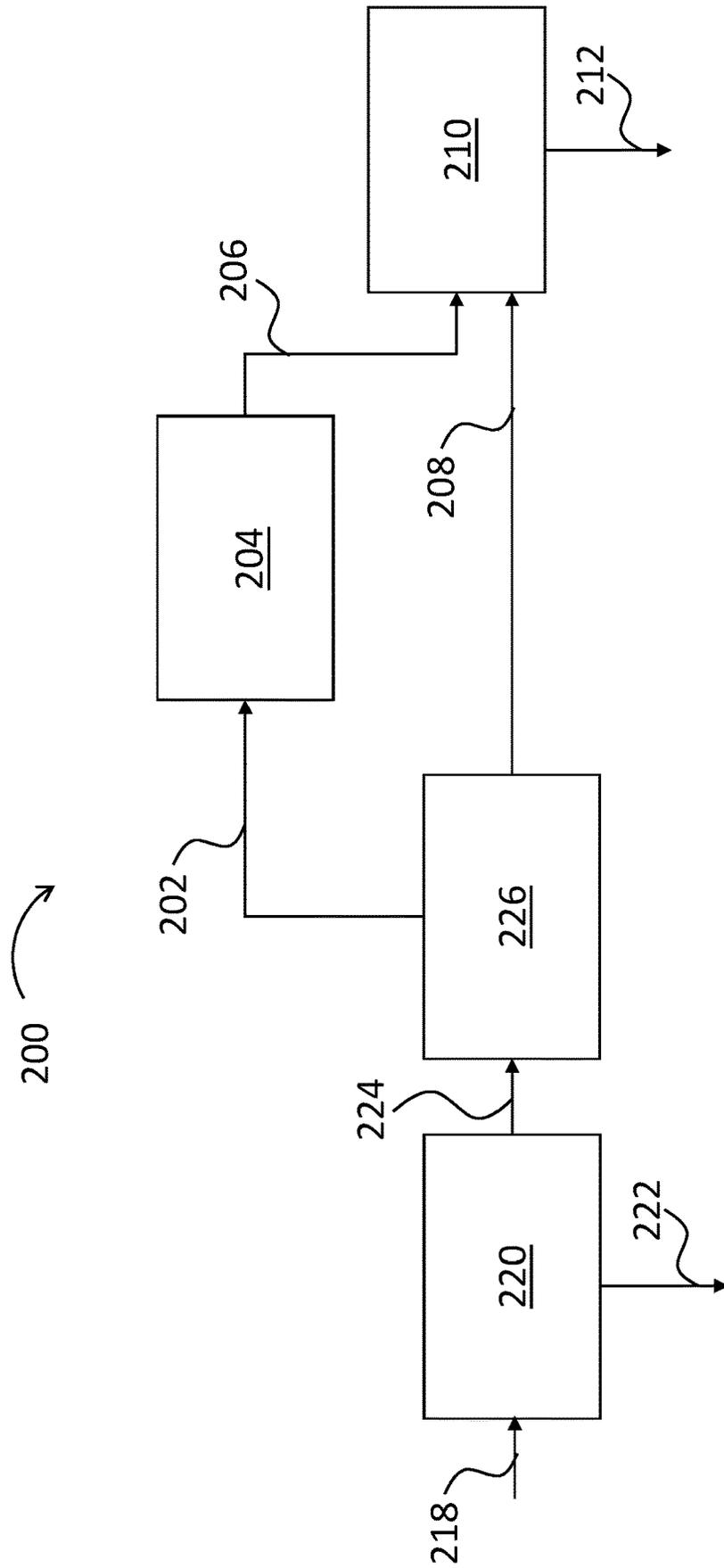


FIG. 2

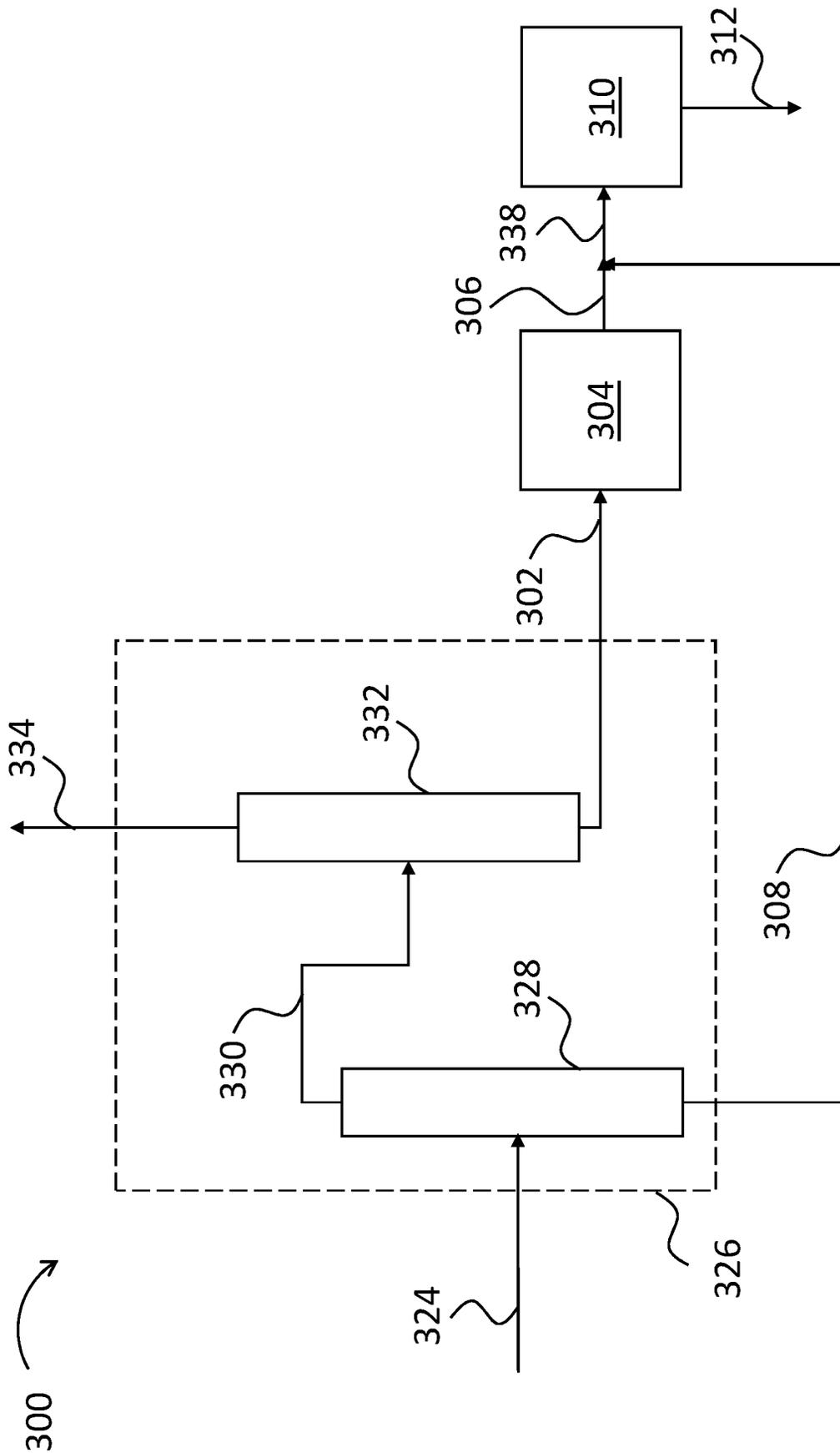


FIG. 3

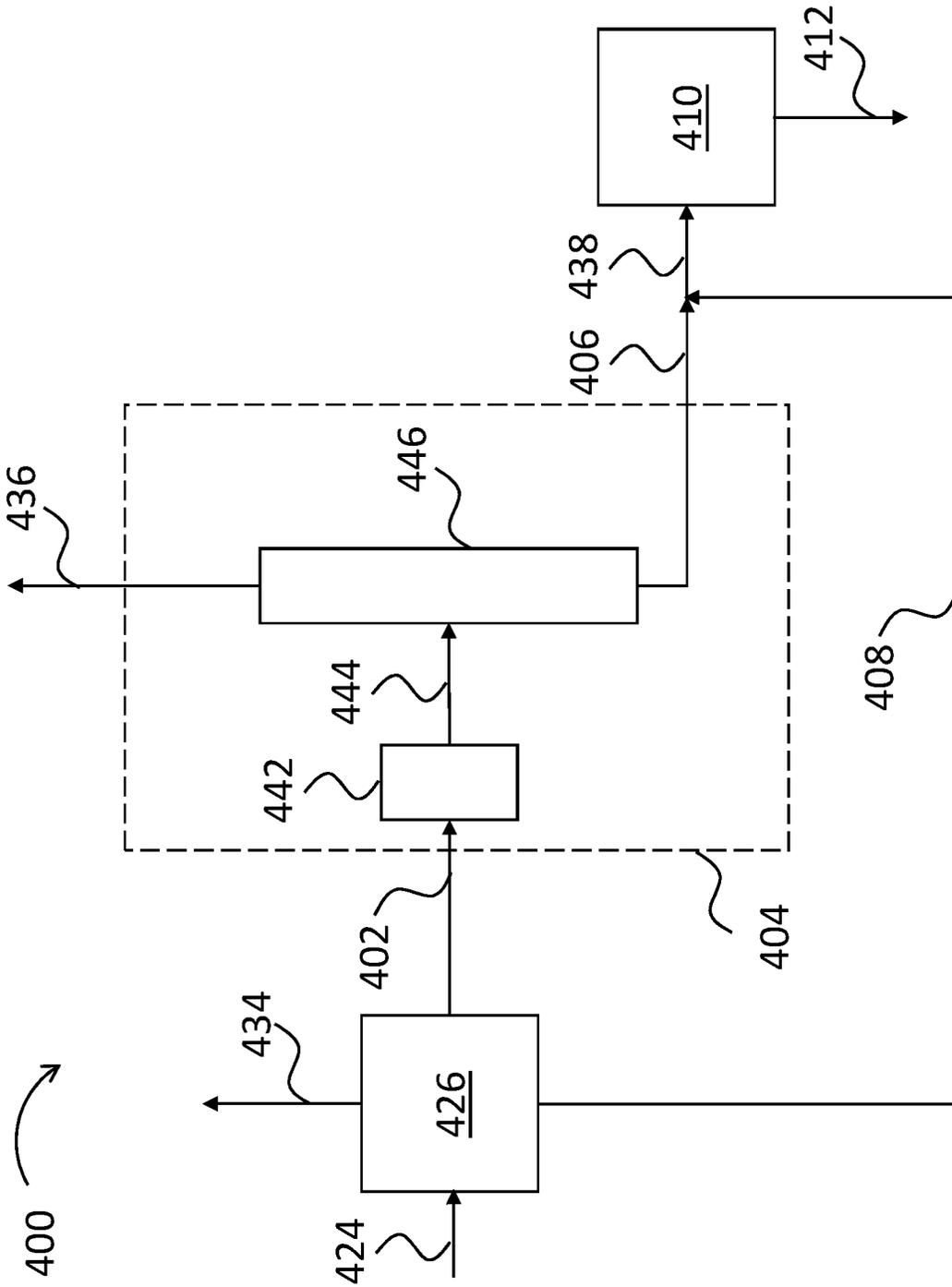


FIG. 4

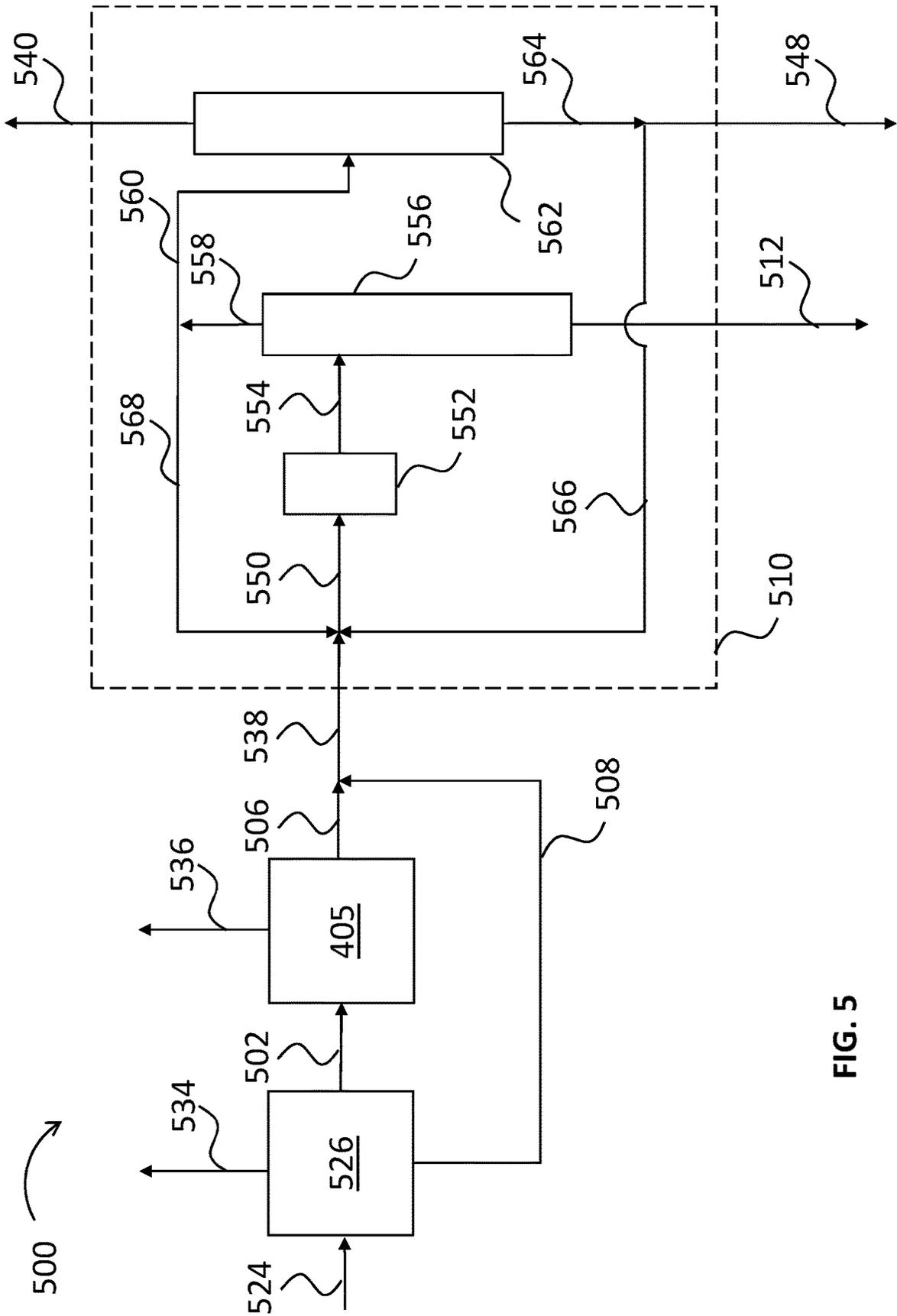


FIG. 5

Analysis	100% JET-A1	JET-A1 / 30% IPB-1	JET-A1 / 70% IPB-1	100 % IPB-1	JET-A1 passing value	JET-A1 Spec	
Appearance	C&B	C&B	C&B	C&B	C&B	C&B ¹	
Acidity, mg KOH/g	0.010	0.010	0.010	0.015	0.015 max	D3242	
Aromatics, vol %	17.1	17.0	8.3	0.245 mM ²	25.0 max	D1319	
Sulfur, total, wt.%	0.0363	0.0255	0.0114	<0.0010	0.30 max	D2622	
Naphthalenes, vol %	1.98				3.0 max	D1840	
Distillation, °C	-	-	-	-	-	D86	
	IBP	160.1	164.3	171.1	176.2	Report	"
	10%	191.6	189.7	187.7	187.5	205 max	"
	20%					Report	"
	50%	220.7	215.8	210.9	206.8	Report	"
	90%	251.8	253.4	257.8	265.3	Report	"
	FBP	269.4	281.8	293.3	303.9	300 max	"
Distill. Resid., vol %	1.0	1.0	1.0	1.2	1.5 max	"	
Distill. Loss, vol %	0.6	0.3	0.8	1.2	1.5 max	"	
Flash Pt., °C	48.9	53.3	54.4	58.8	38 min	D56	
Density, kg/m ³	823.8	806.8	784.8	767.0	775 - 840	D4052	
Freeze Pt., °C	-63.0	-64.0	-57.0	-56.0	-47 max	D2386	
Viscosity, -20 °C, cSt	5.954	5.383	5.731	6.058	8.0 max	D445	
Heat of Comb, MJ/kg	43.08	43.21	43.61	43.73	42.8 min	D3338	
Smoke Pt., mm	22.0*	28.0	39.0	45.0	25.0 min	D1322	
Copper Corrosion	1a	1a	1a	1a	1 max	D130	
JFTOT breakpoint, °C	270	270	285	295	260 min	D3241	
Ext gum mg/100mL	2	1	2	2	7 max	D381	
Hydrogen Cont, wt %	13.57	13.85	14.53	14.51	13.40 min	D3343	
MSEP	96	93	96	100	90 min	D3948	
Electric Cond., pS/m	<1	<1	<1	<1	150-450	D2642	
Peroxides, mg/kg				0.9	x	D3703	
Cetane Number				48.2	x	D613	
	Items in BOLD & Italics do not meet JET-A1 specifications						

1 – C&B refers to “clear and bright”

2 – This value determined according to M-1514

* - Smoke point below 25 meets specification when the naphthalene content is less than 3.0 vol%

FIG. 6

Analysis	100% JET-A1	JET-A1 / 30% IPB-2	JET-A1 / 70% IPB-2	100 % IPB-2	JET-A1 passing value	JET-A1 Spec
Appearance	C&B	C&B	C&B	C&B	C&B	C&B ¹
Acidity, mg KOH/g	0.010	0.014	0.011	0.010	0.015 max	D3242
Aromatics, vol %	17.1	16.8	7.2		25.0 max	D1319
Sulfur, total, wt.%	0.0363	0.0286	0.0114	<0.0010	0.30 max	D2622
Naphthalenes, vol %	1.98	1.42			3.0 max	D1840
Distillation, °C	-	-	-	-	-	D86
	160.1	155.4	151.1	151.9	176.2	Report
	191.6	177.9	169.3	164.6	187.5	205 max
						Report
	220.7	213.4	205.8	197.1	206.8	Report
	251.8	250.7	253.3	250.1	265.3	Report
	269.4	276.6	284.6	293.1	303.9	300 max
Distill. Resid., vol %	1.0	1.3	1.0	1.1	1.5 max	"
Distill. Loss, vol %	0.6	1.3	1.5	1.0	1.5 max	"
Flash Pt., °C	48.9	47.8	45.6	43.3	38 min	D56
Density, kg/m ³	823.8	804.8	778.7	758.2	775 - 840	D4052
Freeze Pt., °C	-63.0	-60.0	-58.0	-62.0	-47 max	D2386
Viscosity, -20 °C, cSt	5.954	5.353	5.445	4.148	8.0 max	D445
Heat of Comb, MJ/kg	43.08	43.28	43.62	44.01	42.8 min	D3338
Smoke Pt., mm	22.0 ³	23.0 ³	40.0	41.0	25.0 min	D1322
Copper Corrosion	1a	1a	1a	1a	1 max	D130
JFTOT breakpoint, °C	270	275	285	>315	260 min	D3241
Ext gum mg/100mL	2	2	1	1	7 max	D381
Hydrogen Cont, wt %	13.57	13.85	14.63	15.12	13.40 min	D3343
MSEP	96	97	96	99.0	90 min	D3948
Electric Cond., pS/m	<1	<1	<1	<1	150-450	D2642
Peroxides, mg/kg				0.6	x	D3703
Cetane Number				47.0	x	D613
	Items in BOLD & Italics do not meet JET-A1 specifications					

FIG. 7

on aromatic rings	Ha	0.17	0.13	0.17	0.15
on olefinic carbons	Hc	0.03	1.29	3.03	4.38
alpha to aromatic rings	H(alpha)	0.16	0.51	1.07	1.49
beta to aromatic rings, naphthenic & paraffinic CH	Hc1	4.94	10.97	19.4	26.06
paraffinic CH2, CH3 beta to and CH2>= gamma from aromatic ring	Hc2	43.3	38.8	32.59	27.69
paraffinic CH3, CH3->gamma from aromatic ring	Hd	51.4	48.29	43.74	40.24
	Celane #	48.8	43.8	36.3	30.8
	CH/CH2	0.11	0.28	0.60	0.94
	CH/CH3	0.10	0.23	0.44	0.65
	CH2/CH3	0.84	0.80	0.75	0.69
	CH3/ (CH2+CH)	1.07	0.97	0.84	0.75
	CH3/CH2	1.19	1.24	1.34	1.45

FIG. 8

**METHODS FOR CONVERTING C2+
OLEFINS TO HIGHER NUMBER OLEFINS
USEFUL IN PRODUCING ISOPARAFFINIC
KEROSENE COMPOSITIONS**

**CROSS REFERENCE TO RELATED
APPLICATIONS**

This application claims the benefit of U.S. Provisional Application Nos. 63/362,565 and 63/362,566, both filed on Apr. 6, 2022, the entire contents of each are incorporated herein by reference.

This application is related to U.S. application Ser. Nos. 17/820,147 and 17/820,159 both filed on Aug. 16, 2022. These U.S. applications are hereby incorporated by reference herein in their entirety.

FIELD OF INVENTION

The present application relates to methods for converting C2+ olefins to higher carbon number olefins. Said higher carbon olefins may be useful for producing isoparaflinic kerosene compositions.

BACKGROUND

Olefins are valued feedstocks in chemical manufacturing. For example, light olefins like ethylene and propylene are useful in polymerization reactions. Higher carbon olefins like C6+ olefins and C8+ olefins, which may be produced by oligomerizing light olefins, are useful in producing specialty surfactants, lubricants, jet/aviation fuel, diesel fuel, fuel additives, and the like. Many oligomerization catalyst systems have been investigated for increasing the yield of preferred higher carbon olefins and with greater yields. However, the steps in upgrading light olefins to higher carbon olefins have remained reasonably unchanged.

SUMMARY OF INVENTION

The present application relates to methods for converting C2+ olefins to higher carbon number olefins.

A nonlimiting example method for producing a blended jet boiling range composition stream comprises: oligomerizing an ethylene stream to a C4+ olefin stream in a first olefin oligomerization unit comprising a serial reactor and a lights removal column, wherein the C4+ olefin stream contains no greater than 10 wt % of methane, ethylene, and ethane combined; wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen; oligomerizing the C4+ olefin stream and a propylene/C4+ olefin stream in a second oligomerization unit to produce an isoolefinic stream; subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as treat gas to produce an isoparaflinic stream having no greater than 10 wt % olefin content; and using least a portion of the isoparaflinic stream to create the blended jet boiling range composition comprising: 30 vol % to 99 vol % of an isoparaflinic blend component sourced from the isoparaflinic stream containing 80 wt % or more of isoparaflins, 5.0 wt % or less of olefins, and 5.0 wt % or less of C19+ hydrocarbons; 1.0 vol % to 70 vol % of a mineral jet boiling range fraction; and a T10 distillation point of 205° C. or less, a

final boiling point of 300° C. or less, a freeze point of -40° C. or lower, and 2.0 wt % or more of C17-C18 hydrocarbons.

A nonlimiting example method for producing a blended jet boiling range composition comprises: providing a raw olefin stream comprising ethylene, propylene and C4+ olefins, wherein at least 10 wt % of all olefins in the raw olefin stream are ethylene, and further containing at least 1000 wppm of each methane and ethane, and at least 100 wppm of each carbon monoxide and hydrogen; subjecting the raw olefin stream to a separation operation to remove hydrogen, carbon monoxide, propylene and C4+ olefins from the raw olefin stream, and produce an ethylene stream containing at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen, wherein at least 95 wt % of all the ethylene in the raw olefin stream is recovered in the ethylene stream; providing at least a portion of the ethylene stream to a first olefin oligomerization unit comprising one or more serial reactors and a lights removal column, to convert in a single pass through the serial reactor(s) at least 90% of the ethylene contained in the ethylene stream to a second C4+ olefin stream containing no greater than 10 wt % of methane, ethylene, and ethane combined; providing at least a portion of each of the propylene and the C4+ olefins removed from the raw olefins stream, and at least a portion of the second C4+ stream to a second olefin oligomerization unit to produce an isoolefinic stream; and subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as treat gas to produce an isoparaflinic stream having no greater than 10 wt % olefin content; and using least a portion of the isoparaflinic stream to create the blended jet boiling range composition comprising: 30 vol % to 99 vol % of an isoparaflinic blend component sourced from the isoparaflinic stream containing 80 wt % or more of isoparaflins, 5.0 wt % or less of olefins, and 5.0 wt % or less of C19+ hydrocarbons; 1.0 vol % to 70 vol % of a mineral jet boiling range fraction; and a T10 distillation point of 205° C. or less, a final boiling point of 300° C. or less, a freeze point of -40° C. or lower, and 2.0 wt % or more of C17-C18 hydrocarbons.

These and other features and attributes of the disclosed methods of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings. The following figures are included to illustrate certain aspects of the disclosure, and should not be viewed as exclusive configurations. The subject matter disclosed is capable of considerable modifications, alterations, combinations, and equivalents in form and function, as will occur to those skilled in the art and having the benefit of this disclosure.

FIG. 1 illustrates a nonlimiting example of a method of the present disclosure.

FIG. 2 illustrates a nonlimiting example of a method of the present disclosure.

FIG. 3 illustrates a nonlimiting example of a method of the present disclosure.

FIG. 4 illustrates a nonlimiting example of a method of the present disclosure.

FIG. 5 illustrates a nonlimiting example of a method of the present disclosure.

FIG. 6 shows compositional information for blends of an isoparaffinic blend component with a conventional jet fuel.

FIG. 7 shows compositional information for blends of another isoparaffinic blend component with a conventional jet fuel.

FIG. 8 shows results from ¹H NMR characterization of isoolefinic and isoparaffinic blend components.

DETAILED DESCRIPTION

The present application relates to methods for converting C2+ olefins to higher carbon number olefins. Said olefins and/or said olefins converted to paraffins may be useful for a variety of other applications including fuels and blendstocks for fuels. More specifically, the conversion may include two oligomerization processes that may advantageously improve the overall ethylene conversion while having flexibility and efficiencies that may provide energy and cost savings.

Definitions

All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

In this discussion, a jet fuel or jet fuel blend component that contains at least a portion of synthesized jet fuel boiling range compounds (i.e., jet boiling range compounds not derived from processing a mineral source) is defined as a synthetic jet fuel or synthetic jet fuel blending component.

In this discussion, if methanol is used as a feedstock for forming olefins, methanol obtained by a variety of processes may be referred to as “sustainable” methanol. Examples of such processes may include, but are not limited to, reforming municipal waste, reforming biomass, fermenting biomass, electrolyzing water to produce hydrogen for reaction with carbon monoxide and/or carbon dioxide, and the like, and any combination thereof.

Current commercial standards for jet fuels typically specify a variety of properties. Examples of property specifications and/or typical properties for commercial jet fuels include a total acidity of 0.1 mg KOH/g or less, or 0.015 mg KOH/g or less, a sulfur content of 3000 wppm or less, a freezing point maximum of -40° C. or -47° C., a viscosity at -20° C. of 8.0 cSt or less, a flash point of at least 38° C., an initial boiling point of 140° C. or more, a T10 distillation point of 205° C. or less, and/or a final boiling point of 300° C. or less. Another example of a property specification is a specification for a maximum deposit thickness on the surface of a heater tube and/or a maximum pressure increase during a thermal stability test at 260° C. (according to ASTM D3241), such as a maximum deposit thickness of 85 nm and/or a maximum pressure increase of 25 mm Hg. Still another example of a property specification can be a water separation rating, such as a water separation rating of 85 or more, as measured according to ASTM D3948. A water separation rating provides an indication of the amount of surfactant present in a jet fuel boiling range sample. Petroleum fractions that have an appropriate boiling range and that also satisfy the various requirements for a commercial standard can be tested (such as according to ASTM D3241) and certified for use as jet fuels. In some aspects, the kerosene boiling range fraction can correspond to a jet fuel fraction that satisfies the specification for a jet fuel under

ASTM D1655. This can include a thermal stability breakpoint of 260° C. or more, or 275° C. or more, as defined by ASTM D3241.

Unless otherwise specified, distillation points and boiling points can be determined according to ASTM D86. It is noted that still other methods of boiling point characterization may be provided in the examples. The values generated by such other methods are believed to be indicative of the values that would be obtained under ASTM D86.

In this discussion, the jet fuel boiling range or kerosene boiling range is defined as 140° C. to 300° C. A jet fuel boiling range fraction or a kerosene boiling range fraction is defined as a fraction with a T10 distillation point of 140° C. to 205° C. or less, and a final boiling point of 300° C. or less. It is noted that jet fuel boiling range fractions can sometimes also have a flash point of 38° C. or higher, although kerosene boiling range fractions do not necessarily have such a requirement.

In this discussion, a hydroprocessed fraction refers to a hydrocarbon fraction and/or hydrocarbonaceous fraction that has been exposed to a catalyst having hydroprocessing activity in the presence of 300 kPa-a or more of hydrogen at a temperature of 200° C. or more. Examples of hydroprocessed fractions include hydroprocessed distillate fractions (i.e., a hydroprocessed fraction having the distillate boiling range), hydroprocessed kerosene fractions (i.e., a hydroprocessed fraction having the kerosene boiling range) and hydroprocessed diesel fractions (i.e., a hydroprocessed fraction having the diesel boiling range). It is noted that a hydroprocessed fraction derived from a biological source, such as hydrotreated vegetable oil, can correspond to a hydroprocessed distillate fraction, a hydroprocessed kerosene fraction, and/or a hydroprocessed diesel fraction, depending on the boiling range of the hydroprocessed fraction.

With regard to characterizing properties of kerosene/jet boiling range fractions and/or blends of such fractions with other components to form kerosene/jet boiling range fuels, a variety of methods can be used. Density of a blend at 15° C. (kg/m³) can be determined according to ASTM D4052. Sulfur (in wppm or wt %) can be determined according to ASTM D2622, while nitrogen (in wppm or wt %) can be determined according to D4629. Kinematic viscosity at either -20° C. or -40° C. (in cSt) can be determined according to ASTM D445. Pour point can be determined according to ASTM D5949. Cloud point can be determined according to D5773. Freeze point can be determined according to D5972. Flash point can be determined according to ASTM D56. Aromatics content can be determined according to ASTM D1319. Cetane number can be determined according to ASTM D613.

In this discussion, the content of n-paraffins, isoparaffins, cycloparaffins, aromatics, and/or olefins can be determined according to test method UOP 990. It is noted that for some of the paraffin, n-paraffin, and isoparaffin contents described below, the contents were determined using gas chromatography according to the Linear Paraffin method. The n-paraffin peaks from a hydrocarbon sample in gas chromatography are well known. The n-paraffin peaks can be separately integrated to determine the n-paraffin content of a sample using gas chromatography. The peaks in a GC spectrum between the n-paraffin peaks can be assigned as isoparaffins with the same carbon number as the lower peak, so that a total amount of paraffins having a given carbon number can be determined. The isoparaffin content for a given carbon number can be determined by subtracting the n-paraffin content from the total paraffin content. It is

believed that the values herein determined by the Linear Paraffin method are representative of the values that would be obtained according to UOP 990.

As noted above, UOP 990 can be used to determine paraffin, naphthene, and aromatics content. It is noted that for some paraffin, naphthene, and/or aromatics contents described herein, supercritical fluid chromatography (SFC) was used. It is believed that the SFC characterization values are representative of what would be obtained according to UOP 990. For SFC characterization, the characterization was performed using a commercial supercritical fluid chromatograph system, and the methodology represents an expansion on the methodology described in ASTM D5186 to allow for separate characterization of paraffins and naphthenes. The expansion on the ASTM D5186 methodology was enabled by using additional separation columns, to allow for resolution of naphthenes and paraffins. The system was equipped with the following components: a high pressure pump for delivery of supercritical carbon dioxide mobile phase; temperature controlled column oven; autosampler with high pressure liquid injection valve for delivery of sample material into mobile phase; flame ionization detector; mobile phase splitter (low dead volume tee); back pressure regulator to keep the CO₂ in supercritical state; and a computer and data system for control of components and recording of data signal. For analysis, approximately 75 milligrams of sample was diluted in 2 milliliters of toluene and loaded in standard septum cap autosampler vials. The sample was introduced based via the high pressure sampling valve. The SFC separation was performed using multiple commercial silica packed columns (5 micron with either 60 or 30 angstrom pores) connected in series (250 mm in length either 2 mm or 4 mm ID). Column temperature was held typically at 35 or 40° C. For analysis, the head pressure of columns was typically 250 bar. Liquid CO₂ flow rates were typically 0.3 ml/minute for 2 mm ID columns or 2.0 ml/minute for 4 mm ID columns. The SFC FID signal was integrated into paraffin and naphthenic regions. In addition to characterizing aromatics according to ASTM D5186, a supercritical fluid chromatograph was used to analyze samples for split of total paraffins and total naphthenes. A variety of standards employing typical molecular types can be used to calibrate the paraffin/naphthene split for quantification.

As used herein, the term “paraffin” refers to saturated hydrocarbons that may be linear or branched. The paraffin may be straight-chain or branched-chain and is considered to be a non-ring compound. “Paraffin” is intended to embrace all structural isomeric forms of paraffins. The term “n-paraffin” has the expected definition of a straight chain alkane (no branches or rings in the carbon chain). The term “isoparaffin” is used herein to refer to any alkane that includes one or more branches in the carbon chain but does not include any ring structures. The term “paraffin” encompasses the terms “n-paraffin” and “isoparaffin.”

In this discussion, the term “iso-olefin” is analogous to “isoparaffin”, but refers to an alkene rather than an alkane. Thus, an iso-olefin is defined as an alkene that includes at least one branch in the carbon chain but that does not include a ring structure.

In this discussion, the term “naphthene” refers to a cycloalkane (also known as a cycloparaffin). Therefore, naphthenes correspond to saturated ring structures. The term naphthene encompasses single-ring naphthenes and multi-ring naphthenes. The multi-ring naphthenes may have two or more rings, e.g., two-rings, three-rings, four-rings, five-rings, six-rings, seven-rings, eight-rings, nine-rings, and

ten-rings. The rings may be fused and/or bridged. The naphthene can also include various side chains, such as one or more alkyl side chains of 1-10 carbons.

In this discussion, the term “saturates” refers to all straight chain, branched, and cyclic paraffins. Thus, saturates correspond to a combination of paraffins and naphthenes.

In this discussion, the term “aromatic ring” means five or six atoms joined in a ring structure wherein (i) at least four of the atoms joined in the ring structure are carbon atoms and (ii) all of the carbon atoms joined in the ring structure are aromatic carbon atoms. Therefore, aromatic rings correspond to unsaturated ring structures. Aromatic carbons can be identified using, for example, ¹³C Nuclear Magnetic Resonance. Aromatic rings having atoms attached to the ring (e.g., one or more heteroatoms, one or more carbon atoms, etc.) but which are not part of the ring structure are within the scope of the term “aromatic ring.” Additionally, it is noted that ring structures that include one or more heteroatoms (such as sulfur, nitrogen, or oxygen) can correspond to an “aromatic ring” if the ring structure otherwise falls within the definition of an “aromatic ring.”

In this discussion, the term “non-aromatic ring” means four or more carbon atoms joined in at least one ring structure wherein at least one of the four or more carbon atoms in the ring structure is not an aromatic carbon atom. Non-aromatic rings having atoms attached to the ring (e.g., one or more heteroatoms, one or more carbon atoms, etc.), but which are not part of the ring structure, are within the scope of the term “non-aromatic ring.”

In this discussion, the term “aromatics” refers to all compounds that include at least one aromatic ring. Such compounds that include at least one aromatic ring include compounds that have one or more hydrocarbon substituents. It is noted that a compound including at least one aromatic ring and at least one non-aromatic ring falls within the definition of the term “aromatics”.

It is noted that that some hydrocarbons present within a feed or product may fall outside of the definitions for paraffins, naphthenes, and aromatics. For example, any alkenes that are not part of an aromatic compound would fall outside of the above definitions. Similarly, non-aromatic compounds that include a heteroatom, such as sulfur, oxygen, or nitrogen, are not included in the definition of paraffins or naphthenes.

As used herein, the term “Cx hydrocarbon” or “Cx” indicates hydrocarbon molecules having the number of carbon atoms represented by the number “x”. The term “Cx+ hydrocarbons” indicates those molecules noted above having the number of carbon atoms represented by the number “x” or greater. For example, “C17+ hydrocarbons” would include C17, C18, and higher carbon number hydrocarbons. Similarly “Cx- hydrocarbons” indicates those molecules noted above having the number of carbon atoms represented by the number “x” or fewer.

Methods and Compositions

FIG. 1 illustrates a nonlimiting example of a method **100** of the present disclosure. The illustrated method **100** includes a first oligomerization **104** and a second oligomerization **110** and, optionally, hydroprocessing **114**. Briefly, an ethylene stream **102** undergoes the first oligomerization **104**, which produces a C4+ olefin stream **106**. The C4+ olefin stream **106** and a propylene/C4+ olefin stream **108** then undergo a second oligomerization **110**. The second oligomerization **110** produces an isoolefinic stream **112**. The isoolefinic stream **112** has many potential uses. In a non-

limiting example, the isoolefinic stream **112** undergoes hydroprocessing **114** and produces an isoparaffinic stream **116**.

The ethylene stream **102** may contain at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen (or (i) at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen, or (ii) at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen). The ethylene may be present in the ethylene stream **102** in an amount of at least 50 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99.9 wt %, or 50 wt % to 99 wt %, or 60 wt % to 95 wt %, or 70 wt % to 90 wt %. The ethane may be present in the ethylene stream **102** in an amount of at least 2000 wppm, or at least 5000 wppm, or at least 1 wt %, or at least 10 wt %, or at least 25 wt %, or at least 45 wt %, or 2000 wppm to 45 wt %, or 2000 wppm to 25 wt %, or 5000 wppm to 10 wt %. The methane may be present in the ethylene stream **102** in an amount of no greater than 1000 wppm, or no greater than 500 wppm, or no greater than 250 wppm, or 10 wppm to 1000 wppm, or 10 wppm to 250 wppm, or 100 wppm to 500 wppm, or 250 wppm to 1000 wppm. Each of carbon monoxide and hydrogen, individually, may be present in the ethylene stream **102** in an amount of no greater than 20 wppm, no greater than 5 wppm, no greater than 1 wppm, or no greater than 0.5 wppm, or no greater than 0.1 wppm, or 0.001 wppm to 20 wppm, or 0.001 wppm to 5 wppm, or 0.001 wppm to 1 wppm, or 0.001 wppm to 0.5 wppm.

The two oligomerizations have similar chemical reactions, but are not identical steps. The chemistries of these steps may be accomplished by very different processes. For example, the first oligomerization **104** may be achieved with high efficiency and efficacy in the liquid phase using a homogenous catalyst. In contrast, the second oligomerization **110** of higher molecular weight olefins, such as propylene and butenes, may be more efficiently and effectively carried out with a heterogeneous catalyst under conditions where some or all of the components are supercritical. By separately oligomerizing the ethylene to a higher molecular weight olefin (the first oligomerization **104**), the resultant olefins may be included as a portion of the feedstock in the second oligomerization **110**, thereby increasing the overall yield of the higher molecular weight olefins (e.g., C10+ olefins). That is, the feedstock for the second oligomerization **110** has minimal amounts of ethylene. Overall, the process may benefit from separately using (a) a first oligomerization catalyst specific to high yields of ethylene oligomerization and (b) second oligomerization catalysts that have high yields of distillate-range olefins from olefin feedstock that has minimal amounts of ethylene. Because the two oligomerizations are completed as separate processes (although said processes may be performed in different portions of the same vessel), the overall methods and systems may have higher yields of distillate-range olefins that may then be used to produce the isoparaffinic stream and additional fuel products (e.g., distillates, jet fuel, kerosene, and the like).

When the ethylene stream **102** undergoes the first oligomerization **104**, at least 95% of the ethylene present in the ethylene stream **102** may be converted to a C4+ olefins (e.g., C4 olefins, C6 olefins, C8 olefins, and C10 olefins). The C4+ olefin stream **106** no greater than 10 wt % of methane,

ethylene, and ethane combined (or (i) no greater than 5 wt % of methane, ethylene, and ethane combined, or (ii) no greater than 2000 wppm of methane, ethylene, and ethane combined, or (iii) no greater than 1000 wppm of methane, ethylene, and ethane combined, or (iv) at least 10 wppm and no greater than 10 wt % (or 2000 wppm, or 1000 wppm) of methane, ethylene, and ethane combined). The C4+ olefins may be present in the C4+ olefin stream **106** in an amount of at least 99 wt %, or at least 99.5 wt %, or at least 99.999 wt %, or 99 wt % to 99.999 wt %

Having a low amount of carbon monoxide and hydrogen in the ethylene stream **102** may allow for high conversion of the ethylene to C4+ olefins in the first oligomerization **104**. For example, carbon monoxide and hydrogen may be deleterious to the catalyst system in the first oligomerization **104**, especially if the first oligomerization **104** utilizes nickel. However, the first oligomerization **104** may largely be unaffected by saturated hydrocarbons like methane and ethane, which may allow for higher concentrations of saturated hydrocarbons.

The ethylene stream **102** may be from any suitable source including, but not limited to, ethylene derived from an ethanol dehydration reaction, a steam cracker, a fluidized catalytic cracker (FCC), a catalytic conversion reaction of methanol typically called "Methanol To Olefins (MTO)," and the like, and any combination of sources. Note that most MTO processes may also satisfactorily convert other alcohols like ethanol or butanol, and/or ethers like dimethyl ether (DME) or diethyl ether (DEE), typically in some proportion with methanol, to useful olefins with the same catalysts and equipment given minor adjustments for rates and/or concentrations of various reaction products and contaminants. Other oxygen containing molecules such as ketones, aldehydes and esters may also be converted to olefins, but not desirably given that their relative hydrogen deficiency to alcohols also produces more carbonaceous coke on the catalysts. Nonetheless, minor quantities of the aforementioned oxygenates are produced by the MTO reaction as byproducts, recovered in some form and recycled back to the MTO reactor in combination with the main alcohol feed. Hence, a more generic term often used for these types of technologies is "oxygenates to olefins."

The first oligomerization **104** may occur in a first oligomerization unit, which may comprise one or more serial reactors, typically fixed bed adiabatic reactors housing (or otherwise containing) the oligomerization catalyst or a continuous stirred tank reactor (CSTR) or pump-around piping system for housing homogenous oligomerization catalysts.

Examples of catalysts used in the first oligomerization **104** may include, but are not limited to, (a) homogenous catalysts including (a1) homogenous catalysts containing organic aluminum, nickel, titanium, and/or zirconium or (a2) Ziegler types where (a1) or (a2) may optionally include a ligand for activating the metal and may optionally include a solvent such as a hydrocarbon or ionic liquid cyclohexane; (b) heterogeneous catalysts such as (b1) solid phosphoric acid, (b2) microporous materials such as zeolites, for example, ZSM-5 catalyst, ZSM-57 catalyst, ZSM-22 catalyst, ZSM-48 catalyst, ZSM-12 catalyst, or (b3) silicoaluminophosphate (SAPO) molecular sieve; (c) the like; and (d) any mixture thereof.

The first oligomerization **104** may utilize a homogeneous organometallic catalyst. This may include, for example, nickel and other metal liganded catalysts as described in "Oligomerization of Monoolefins by Homogeneous Catalysts," A. Forestière, et al., *Oil & Gas Science and Technology—Rev. IFP*, Vol. 64 (2009), No. 6, pp. 649-667.

Limiting the concentration of C10+ olefins to minor amounts (e.g. no more than about 15 wt % of the total C4+ oligomer product) may be optimal for feeding the stream to the second oligomerization **110**. This may be achieved using ethylene oligomerization processes offered for license by IFP (now Axens) called DIMERSOL-E®, and that offered for license by UOP called Linear-1®. The second oligomerization **110** may function acceptably well with C10+ olefins in the reactor system feed, but may function most efficiently with a relatively low concentration of those components. A C10+ molecule is already in the carbon number range of distillate products such as diesel and jet fuel, so the main benefit of feeding it to the second oligomerization **110** is to provide the molecule with an alkyl branch (through adding a lighter olefin) to decrease its freeze point, at the risk of increased deleterious cracking reactions to which higher carbon number olefins are susceptible.

Contact between the ethylene stream **102** and the first oligomerization catalyst may be under conditions suitable for oligomerizing ethylene. For example, the temperature may be about 25° C. to about 300° C. (or about 50° C. to about 200° C.). For example, the pressure may be about 100 psia to about 2000 psia (or about 200 psia to about 1200 psia, or about 250 psia to about 1000 psia).

The propylene/C4+ olefin stream **108** and the C4+ olefin stream **106** undergo the second oligomerization **110** (e.g., in a second oligomerization unit) to produce the isoolefinic stream **112**. While illustrated as entering the second oligomerization **110** separately, the method may include mixing (or otherwise blending) the propylene/C4+ olefin stream **108** and the C4+ olefin stream **106** before undergoing the second oligomerization **110**.

The second oligomerization **110** that produces the isoolefinic stream **112** may optionally utilize the process described in U.S. Pat. No. 7,692,049, which is incorporated by reference in its entirety.

The propylene/C4+ olefin stream **108** may contain any single C3 to C9 olefin or any mixture thereof in any proportion. The propylene/C4+ olefin stream **108** may contain at least 50 wt % C3+ olefins. The C3+ olefins may be present in the propylene/C4+ olefin stream **108** in an amount of at least 50 wt %, at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 95 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 95 wt %. The distribution of carbon numbers for the C3+ olefins may vary based on the source of the propylene/C4+ olefin stream **108**. For example, the propylene/C4+ olefin stream **108** may comprise at least 5 wt % propylene, at least 5 wt % C4 olefin, and C5+ olefins such that the C3+ olefin concentration is at least 50 wt % of the propylene/C4+ olefin stream **108**. C3 olefins may be present in the propylene/C4+ olefin stream **108** in an amount of at least 5 wt %, at least 10 wt %, or at least 20 wt %, or at least 30 wt %, or at least 40 wt %, or 5 wt % to 80 wt %, or 5 wt % to 30 wt %, or 10 wt % to 50 wt %, or 25 wt % to 75 wt %, or 40 wt % to 80 wt % of the propylene/C4+ olefin stream **108**. C4 olefins may be present in the propylene/C4+ olefin stream **108** in an amount of at least 5 wt %, at least 10 wt %, or at least 20 wt %, or at least 30 wt %, or at least 40 wt %, or 5 wt % to 80 wt %, or 5 wt % to 30 wt %, or 10 wt % to 50 wt %, or 25 wt % to 75 wt %, or 40 wt % to 80 wt % of the

propylene/C4+ olefin stream **108**. C6 olefins may be present in the propylene/C4+ olefin stream **108** in an amount of at least 5 wt %, at least 10 wt %, or at least 20 wt %, or at least 30 wt %, or at least 40 wt %, or 5 wt % to 80 wt %, or 5 wt % to 30 wt %, or 10 wt % to 50 wt %, or 25 wt % to 75 wt %, or 40 wt % to 80 wt % of the propylene/C4+ olefin stream **108**. In a nonlimiting example, the propylene/C4+ olefin stream **108** may comprise propylene, at least 5 wt % C4 olefins, at least 40 wt % C5 olefins, and at least 10 wt % C6 olefins. In another nonlimiting example, the propylene/C4+ olefin stream **108** may comprise propylene, at least 20 wt % C4 olefins, at least 40 wt % C5 olefins, and at least 10 wt % C6 olefins. In yet another nonlimiting example, the propylene/C4+ olefin stream **108** may comprise propylene, at least 40 wt % C4 olefins, at least 40 wt % C5 olefins, and at least 10 wt % C6 olefins.

The propylene/C4+ olefin stream **108** may be from any suitable source including, but not limited to, C4+ byproducts derived from a propane dehydrogenation reactor, a butane dehydrogenation reactor, a steam cracker, a fluidized catalytic cracker (FCC), a catalytic conversion reaction of methanol typically called "Methanol To Olefins (MTO), the like, and any combinations of sources.

The second oligomerization **110** may occur in an oligomerization unit, which may comprise a fixed bed adiabatic reactor housing (or otherwise containing) the oligomerization catalyst or an isothermal tubular reactor housing (or otherwise containing) the oligomerization catalyst.

Examples of oligomerization catalysts that may be used in the second oligomerization **110** may include, but are not limited to, the zeolite families respectively comprising, MWW family (e.g., MCM-22), *BEA family (e.g., zeolite beta), FAU catalyst, MTW family (e.g., ZSM-12), TON family (e.g., ZSM-22), MTT family (e.g., ZSM-23), *MRE family (e.g., ZSM-48), MFS family (e.g., ZSM-57), SAPO molecular sieves, the like, and any mixture thereof.

Contacting the propylene/C4+ olefin stream **108** and the C4+ olefin stream **106** (introduced as a mixture or separately) with the second oligomerization catalyst may be under conditions suitable for oligomerizing olefins. For example, the temperature may be about 150° C. to about 300° C. (or about 150° C. to about 250° C., or about 200° C. to about 300° C.). For example, the pressure may be about 600 psia to about 2000 psia (or about 600 psia to about 1200 psia, or about 1000 psia to about 2000 psia).

The second oligomerization unit or a unit between the second oligomerization unit and the hydroprocessing unit may remove at least one light olefin (e.g., C3-C9 olefins, or C3 to C6 olefins, or C3 to C8 olefins) stream from the isoolefinic stream **112**. Said light olefins may be recycled back as a portion of the feed to the oligomerization unit along with the propylene/C4+ olefin stream **108** and the C4+ olefin stream **106**.

The second oligomerization **110** generates an isoolefinic stream **112**. The composition of the isoolefinic stream **112** depends on, among other things, the conditions for the second oligomerization **110**, the composition of the propylene/C4+ olefin stream **108**, the composition of the C4+ olefin stream **106**, and the catalyst.

The isoolefinic stream **112** may contain predominantly C6+ olefins (or C8+ olefins, or C9+ olefins). For example, the isoolefinic stream **112** may contain at least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) C6+ olefins (e.g., C6 to C20 olefins)

with no greater than 20 wt % C5- olefins (or no greater than 10 wt % C5- olefins, or no greater than 5 wt % C5- olefins). In another example, the isoolefinic stream **112** may contain at least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) C8+ olefins (e.g., C8 to C20 olefins) with no greater than 20 wt % C7- olefins (or no greater than 10 wt % C7- olefins, or no greater than 5 wt % C7- olefins). In yet another example, the isoolefinic stream **112** may contain at least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) C9+ olefins (e.g., C9 to C20 olefins) with no greater than 20 wt % C8- olefins (or no greater than 10 wt % C8- olefins, or no greater than 5 wt % C8- olefins).

At least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) of the olefins in the isoolefinic stream **112** may be isoolefinic.

For example, 80 wt % or more of the isoolefinic stream **112**, or 90 wt % or more, or 94 wt % or more, or 97 wt % or more, may be composed of C9 to C20 isoolefins. Further, 2.0 wt % to 25 wt % of the isoolefinic stream **112** may be composed of C9 olefins (e.g., C9 isoolefins), or 2.0 wt % to 15 wt %, or 5.0 wt % to 25 wt %, or 5.0 wt % to 15 wt %, or 2.0 wt % to 10 wt %. Further, 1.0 wt % to 15 wt % of the isoolefinic stream **112** may be composed of C17+ olefins (e.g., C17+ isoolefins), or 2.5 wt % to 15 wt %. In some aspects, 1.0 wt % to 15 wt % of the isoolefinic stream **112** may be composed of C17 and/or C18 olefins (e.g., C17 and/or C18 isoolefins), or 2.5 wt % to 15 wt %, or 1.0 wt % to 10 wt %, or 2.5 wt % to 10 wt %. Further, the isoolefinic stream **112** may contain 5.0 wt % or less of C19+ olefins (e.g., C19+ isoolefins), or 3.0 wt % or less, or 1.0 wt % or less, such as down to having substantially no content of C19+ hydrocarbons. Further, the isoolefinic stream **112** may include 5.0 wt % or less of C8- olefins, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, such as down to 0.1 wt % or possibly still lower (i.e., substantially no C8- olefins).

In another example, the isoolefinic stream **112** can contain 60 wt % to 90 wt % of C11 to C18 olefins (e.g., C11 to C18 isoolefins). Additionally or alternately, the isoolefinic stream **112** may contain 50 wt % to 75 wt % of C12 to C16 olefins (e.g., C12 to C16 isoolefins). This is particularly advantageous for being suitable for further processing (e.g., hydroprocessing) where the resultant product is flexible for use as an aviation or diesel fuel.

The isoolefinic stream **112** may contain a reduced or minimized amount of aromatics. This can correspond to containing 5.0 wt % or less of aromatics, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, or 0.1 wt % or less, such as down to having substantially no aromatics content.

The composition of the isoolefinic stream **112**, or a portion or fraction thereof, may be a suitable product for use in a variety of applications or suitable for further processing to suitable product for use in a variety of applications. For example, the isoolefinic stream **112** may be suitable for further processing to produce a blend composition (e.g., jet fuel blend stock, diesel fuel blend stock, distillate blend stock, kerosene blend stock, and the like), specialty chemicals (e.g., surfactants, lubricants, solvents, hydraulic and other working fluids, and the like), and the like. In a nonlimiting example, a portion or all of the isoolefinic

stream **112** may be further subjected to hydroprocessing **114** to create the isoparaffinic stream **116** (preferably having no greater than 10 wt % olefin content).

Mild hydroprocessing can generally convert iso-olefins to isoparaffins with a reduced or minimized amount of reduction in the size of the carbon chains in a fraction. In addition to converting iso-olefins to isoparaffins, hydroprocessing of a kerosene fraction can also be used to remove sulfur, remove nitrogen, saturate olefins, saturate aromatics, and/or for other purposes.

During hydroprocessing, a feedstock that is partially or entirely composed of a jet fuel boiling range fraction is treated in a hydrotreatment (or other hydroprocessing) reactor that includes one or more hydrotreatment stages or beds. Optionally, the reaction conditions in the hydrotreatment stage(s) can be conditions suitable for reducing the sulfur content of the feedstream, such as conditions suitable for reducing the sulfur content of the feedstream to 500 wppm or less, or 100 wppm or less, or 10 wppm or less, such as down to 0.5 wppm or possibly still lower. The reaction conditions can include an LHSV of 0.1 to 20.0 hr⁻¹, a hydrogen partial pressure from about 50 psig (0.34 MPag) to about 3000 psig (20.7 MPag), a treat gas containing at least about 50% hydrogen, and a temperature of from about 450° F. (232° C.) to about 800° F. (427° C.). Preferably, the reaction conditions include an LHSV of from about 0.3 to about 5 hr⁻¹, a hydrogen partial pressure from about 100 psig (0.69 MPag) to about 1000 psig (6.9 MPag), and a temperature of from about 700° F. (371° C.) to about 750° F. (399° C.).

Optionally, a hydrotreatment reactor can be used that operates at a relatively low total pressure values, such as total pressures of about 200 psig (1.4 MPag) to about 800 psig (5.5 MPag). For example, the pressure in a stage in the hydrotreatment reactor can be at least about 200 psig (1.4 MPag), or at least about 300 psig (2.1 MPag), or at least about 400 psig (2.8 MPag), or at least about 450 psig (3.1 MPag). The pressure in a stage in the hydrotreatment reactor can be about 800 psig (5.5 MPag) or less, or about 700 psig (4.8 MPag) or less, or about 600 psig (4.1 MPa) or less.

The catalyst in a hydrotreatment stage can be a conventional hydrotreating catalyst, such as a catalyst composed of a Group VIB metal and/or a Group VIII metal on a support. Suitable metals include cobalt, nickel, molybdenum, tungsten, or combinations thereof. Preferred combinations of metals include nickel and molybdenum or nickel, cobalt, and molybdenum. Suitable supports include silica, silica-alumina, alumina, and titania.

The isoparaffinic stream **116** resulting from hydroprocessing **114** may be suitable for creating blend compositions (e.g., jet fuel blend stock, diesel fuel blend stock, distillate blend stock, kerosene blend stock, and the like). Advantageously, the isoolefinic stream **112** and the resultant isoparaffinic stream **116** may have a low aromatic content, which may be advantageous for producing low aromatic content fuels (e.g. jet fuels, jet fuel blend stocks).

The isoparaffinic stream **116** may have a similar carbon number distribution to the isoolefinic stream **112** but as paraffins rather than olefins. Therefore, the isoparaffinic stream **116** may contain predominantly C6+ isoparaffins (or C8+ isoparaffins, or C9+ isoparaffins). For example, the isoparaffinic stream **116** may contain at least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) C6+ paraffins (e.g., C6 to C20 paraffins) with no greater than 20 wt % C5- paraffins (or no

greater than 10 wt % C5- paraffins, or no greater than 5 wt % C5- paraffins). In another example, the isoparaffinic stream **116** may contain at least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) C8+ paraffins (e.g., C8 to C20 paraffins) with no greater than 20 wt % C7-paraffins (or no greater than 10 wt % C7- paraffins, or no greater than 5 wt % C7- paraffins). In yet another example, the isoparaffinic stream **116** may contain at least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) C9+ paraffins (e.g., C9 to C20 paraffins) with no greater than 20 wt % C8- paraffins (or no greater than 10 wt % C8-paraffins, or no greater than 5 wt % C8- paraffins).

At least 50 wt % (or at least 60 wt %, or at least 70 wt %, or at least 80 wt %, or 50 wt % to 99 wt %, or 50 wt % to 80 wt %, or 60 wt % to 90 wt %, or 70 wt % to 90 wt %, or 80 wt % to 99 wt %, or 94 wt % to 99 wt %) of the paraffins in the isoparaffinic stream **116** may be isoparaffinic.

For example, 80 wt % or more, or 94 wt % or more, or 97 wt % or more, may be composed of C9 to C20 isoparaffins. Further, 2.0 wt % to 25 wt % of the isoparaffinic stream **116** may be composed of C9 paraffins (e.g., C9 isoparaffins), or 2.0 wt % to 15 wt %, or 5.0 wt % to 25 wt %, or 5.0 wt % to 15 wt %, or 2.0 wt % to 10 wt %. Further, 1.0 wt % to 15 wt % of the isoparaffinic stream **116** may be composed of C17+ paraffins (e.g., C17+ isoparaffins), or 2.5 wt % to 15 wt %. In some aspects, 1.0 wt % to 15 wt % of the isoparaffinic stream **116** may be composed of C17 and/or C18 paraffins (e.g., C17 and/or C18 isoparaffins), or 2.5 wt % to 15 wt %, or 1.0 wt % to 10 wt %, or 2.5 wt % to 10 wt %. Further, the isoparaffinic stream **116** may contain 5.0 wt % or less of C19+ paraffins (e.g., C19+ isoparaffins), or 3.0 wt % or less, or 1.0 wt % or less, such as down to having substantially no content of C19+ hydrocarbons. Further, the isoparaffinic stream **116** may include 5.0 wt % or less of C8- paraffins, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, such as down to 0.1 wt % or possibly still lower (i.e., substantially no C8- paraffins).

In another example, the isoparaffinic stream **116** can contain 60 wt % to 90 wt % of C11 to C18 paraffins (e.g., C11 to C18 isoparaffins). Additionally or alternately, the isoparaffinic stream **116** may contain 50 wt % to 75 wt % of C12 to C16 paraffins (e.g., C12 to C16 isoparaffins). This is particularly advantageous for being suitable for further processing (e.g., hydroprocessing) where the resultant product is flexible for use as an aviation or diesel fuel.

The isoparaffinic stream **116** may contain a reduced or minimized amount of aromatics. This can correspond to containing 5.0 wt % or less of aromatics, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, or 0.1 wt % or less, such as down to having substantially no aromatics content.

While the description of FIG. 1 provides nonlimiting examples of sources for the ethylene stream **102** and the propylene/C4+ olefin stream **108**, FIG. 1 does not illustrate said sources. FIG. 2 illustrates a nonlimiting example that includes a process for converting an oxygenate to olefin then separating of the olefin product to yield potential sources for both the ethylene stream and the propylene/C4+ olefin stream.

FIG. 2 illustrates a nonlimiting example method **200** of the present disclosure showing an oxygenate to olefin reaction **220**, followed by separation **226** of the product from the

oxygenate to olefin process **220**, a first oligomerization **204**, and a second oligomerization **210**. Briefly, an oxygenate stream **218** (e.g., comprising methanol and, optionally, dimethyl ether) undergoes an oxygenate to olefin reaction **220**, which produces a water stream **222** and a raw olefin stream **224**. The raw olefin stream **224** then undergoes separation **226** into an ethylene stream **202** and a propylene/C4+ olefin stream **208**. The ethylene stream **202** then undergoes a first oligomerization **204** to yield a C4+ olefin stream **206**. The propylene/C4+ olefin stream **208** and C4+ olefin stream **206** may then be used in a variety of applications. In the illustrated example, the propylene/C4+ olefin stream **208** and C4+ olefin stream **206** are inputs for a second oligomerization **210** to produce an isoolefinic stream **212**. In alternative embodiments, the second oligomerization may be excluded, and the propylene/C4+ olefin stream **208** and C4+ olefin stream **206** may be used as feeds for other processes.

The oxygenate stream **218** may be from any suitable source. In nonlimiting examples, the oxygenate (e.g., methanol) may be produced from reforming natural gas, reforming coal, reforming municipal waste, reforming biomass, fermenting biomass, electrolyzing water to produce hydrogen for reaction with carbon monoxide and/or carbon dioxide, and the like, and any combination thereof. Generally, electrolyzing water produces hydrogen and oxygen. The hydrogen may then be reacted with carbon monoxide and/or carbon dioxide to produce methanol.

Examples of methanol conversion catalysts that may be utilized in the oxygenate to olefin reaction **220** may include, but are not limited to, microporous materials, such as zeolites, SAPOs and ALPO materials. Such materials may include, but are not limited to, the zeolite families respectively comprising, MWW family (e.g., MCM-22), *BEA family (e.g., zeolite beta), ZSM-11, (MEL) family (e.g., ZSM-12), TON family (e.g., ZSM-22), MTT family (e.g., ZSM-23), *MRE family (e.g., ZSM-48), MFS family (e.g., ZSM-57), ZSM-5 (MFI), ALPO-18 (AEI) and SAPO-34 (CHA) or their mixtures (including intergrowths).

Contact of the oxygenate stream **218** with the methanol conversion catalyst may be under conditions suitable for producing olefins. For example, the inlet temperature may be about 300° C. to about 625° C. (or about 400° C. to about 600° C., or about 450° C. to about 550° C.). For example, the pressure may be about 20 psia to about 300 psia (or about 30 psia to about 250 psia, or about 50 psia to about 150 psia).

The oxygenate to olefin reaction **220** may occur in a fixed bed adiabatic reactor that houses (or otherwise containing) the methanol conversion catalyst and accepts an input of a oxygenate stream **218**.

A resulting raw olefin stream **224** may comprise ethylene, propylene, and C4+ olefins, wherein at least 10 wt % of all olefins in the stream may be ethylene. The raw olefin stream **224** may further comprise at least 1000 wppm each of methane and ethane, and at least 100 wppm each of carbon monoxide and hydrogen. In other aspects, the raw olefin stream **224** may include other components within the volatility range from hydrogen to butanes, such as propane or dimethyl ether. The exact composition of the raw olefin stream **224** will depend on the specific method of producing the raw olefin stream **224**, and further on the specific means of operating those methods.

The raw olefin stream **224** may have been treated (e.g., in a unit in which the oxygenate to olefin reaction **220** occurs or downstream thereof) by various methods to remove some of the byproducts generated by a given method of producing olefins. Such methods and related systems may be employed on the raw olefin stream **224** within the scope of the present

disclosure, but are not shown in FIG. 2. Examples of such methods may include, but are not limited to, reactor effluent quenching and bulk water removal, gas compression, washing with a caustic solution to remove carbon dioxide, gas drying to bone dry, separation of C5+ species from C4 species, or selective saturation with hydrogen to remove acetylene and methylacetylene, among others well documented in the art. The present disclosure may be readily adapted by one skilled in the art to use the raw olefin stream 224 derived from a wide range of olefin production processes. It may also be useful to combine olefin streams from different sources or processes. In a nonlimiting example, ethylene derived from an ethanol dehydration reaction may be combined with hydrogen, CO, propylene, unreacted propane and C4+ byproducts derived from a propane dehydrogenation reaction to create the raw olefin stream 224.

The raw olefin stream 224 then undergoes separation 226 to produce the ethylene stream 202 and the propylene/C4+ olefin stream 208. The separation 226 may occur in a separation system. Examples of separation apparatuses that may be included in the separation system may include, but are not limited to, fractionators, membranes, the like, and any combination thereof.

The separation 226 may occur in the same unit as the oxygenate to olefin reaction 220 or in a downstream unit.

The separation 226 involves differences in component volatility using equipment such as flash drums and distillation columns, which may be configured in a number of ways to create an ethylene stream 202 that exits the separation 226. From the raw olefin stream 224, hydrogen, carbon monoxide, propylene, and C4+ olefins may be separated out to produce the ethylene stream 202. The ethylene stream 202 may contain at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen (or (i) at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen, or (ii) at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen), and at least 95 wt % of all the ethylene in the raw olefin stream 224 may be recovered in the ethylene stream 202. The ethylene stream 202 may also contain at least 90% of the ethane present in the raw olefin stream 224. Separation 226 creates a separate line for the lower volatility components separated from the ethylene and ethane in the ethylene stream 202, such as propylene and C4+ olefins, which exits the separation as propylene/C4+ olefin stream 208. The separation process may also include membrane and absorption systems instead of or in addition to distillation towers. The compositional description of ethylene stream 102 of FIG. 1 applies to the ethylene stream 202 of FIG. 2.

FIG. 2 illustrates the propylene/C4+ olefin stream 208 after the separation 226 as a single stream, but the propylene/C4+ olefin stream 208 may be two separate streams (e.g., a first stream comprising relatively pure propylene and a second stream comprising relatively pure C4+ olefin). This additional separation may be performed with additional distillation columns, and may include separation of propylene from propane and components of similar or lower volatility like dimethyl ether. This process, known in the art as a "Propylene Concentrator," is particularly useful if the source of olefins is oxygenate conversion that can make significant amounts of dimethyl ether, or catalytic cracking

that can make significant amounts of propane, both of which are not particularly desirable to provide to the optional second oligomerization 210.

The disclosure of FIG. 1 for the ethylene stream 102, the first oligomerization 104, the C4+ olefin stream 106, the propylene/C4+ olefin stream 108, the second oligomerization 110, and isoolefinic stream 112 apply to the ethylene stream 202, the first oligomerization 204, the C4+ olefin stream 206, the propylene/C4+ olefin stream 208, the second oligomerization 210, and isoolefinic stream 212 of FIG. 2. Further, embodiments may include further processing isoolefinic stream 212 as discussed relative to the further processing of isoolefinic stream 112 including hydroprocessing to produce an isoparaffinic stream.

FIG. 3 illustrates a nonlimiting example of a method 300 of the present disclosure where a nonlimiting example separation 326 is described. The disclosure relating to steps, streams, processes, units, etc. with reference numbers with the final two numbers corresponding to a foregoing reference number in FIG. 1 and/or FIG. 2 (e.g., propylene/C4+ olefin stream 108) applies to the corresponding steps, streams, processes, units, etc. having reference numbers with the same final two numbers in FIG. 3 (e.g., propylene/C4+ olefin stream 308). However, the separation 326 illustrated in FIG. 3 is a nonlimiting example of a separation and is one of many possible separations that may be used in separations shown in any of the other FIGS. in the present disclosure.

As illustrated, a raw olefin stream 324 undergoes separation 326 to remove hydrogen, carbon monoxide, propylene and C4+ olefins from the ethylene and ethane. Briefly, the separation 326 creates three separate streams where (1) the higher volatility components (e.g., methane, hydrogen, and carbon monoxide) form a high volatility stream 334, (2) the lower volatility components (e.g., propylene and C4+ olefins) form a propylene/C4+ olefin stream 308, and (3) the intermediate volatility components (e.g., ethylene and ethane) form the ethylene stream 302.

In the separation 326, the raw olefin stream 324 is first introduced to a deethanizer distillation column 328 that separates the lower volatility components (e.g., propylene and C4+ olefins) from the higher and intermediate volatility components (e.g., ethylene, ethane, methane, carbon monoxide, and hydrogen) to yield the propylene/C4+ olefin stream 308 and a first overhead stream 330, respectively. The first overhead stream 330 is then directed to a demethanizer distillation column 332 to separate the higher volatility components from the intermediate volatility components to yield the high volatility stream 334 and the ethylene stream 302. The ethylene stream 302 may contain at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen (or (i) at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen, or (ii) at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen), and at least 95 wt % of all the ethylene in the raw olefin stream 324 may be recovered in the ethylene stream 302. In this embodiment, the ethylene stream 302 may also contain at least 90% of the ethane present in the raw olefin stream in line 324, which eliminates the need for a distillation column serving to separate ethylene from ethane (known in the art as a "C2 Splitter").

The ethylene stream 302 then undergoes a first oligomerization 304, which produces a C4+ olefin stream 306. The

C4+ olefin stream **306** and the propylene/C4+ olefin stream **308** are then used as feed in the second oligomerization **310**. As illustrated, the C4+ olefin stream **306** combines with the propylene/C4+ olefin stream **308** into a feed stream **338**, which enters the second oligomerization **310**. The second oligomerization **310** generates the desired isoolefinic stream **312**. Further, embodiments may include further processing isoolefinic stream **312** as discussed relative to the further processing of isoolefinic stream **112** including hydroprocessing to produce an isoparaffinic stream.

FIG. 4 illustrates a nonlimiting example of a method **400** of the present disclosure where a nonlimiting example first oligomerization **404** is described. The disclosure relating to steps, streams, processes, units, etc. with reference numbers with the final two numbers corresponding to a foregoing reference number in FIG. 1, FIG. 2, and/or FIG. 3 (e.g., propylene/C4+ olefin stream **108**) applies to the corresponding steps, streams, processes, units, etc. having reference numbers with the same final two numbers in FIG. 3 (e.g., propylene/C4+ olefin stream **308**). However, the first oligomerization **404** illustrated in FIG. 4 is a nonlimiting example of a separation and is one of many possible separations that may be used in separations shown in any of the other FIGS. in the present disclosure.

Briefly, the raw olefin stream **424** undergoes a separation **426** to create at least two streams: an ethylene stream **402** and a propylene/C4+ olefin stream **408**, and, optionally, a high volatility stream **434** (for example, when the separation **426** occurs according to the separation **326** of FIG. 3). The ethylene stream **402** then undergoes a first oligomerization **404**, which may convert at least 95% of the ethylene present in the ethylene stream **402** to a C4+ olefin stream **406**. The C4+ olefin stream **406** may contain no greater than 10 wt % of methane, ethylene, and ethane combined (or (i) no greater than 5 wt % of methane, ethylene, and ethane combined, or (ii) no greater than 2000 wppm of methane, ethylene, and ethane combined, or (iii) no greater than 1000 wppm of methane, ethylene, and ethane combined, or (iv) at least 10 wppm and no greater than 10 wt % (or 2000 wppm, or 1000 wppm) of methane, ethylene, and ethane combined). The C4+ olefin stream **406** and the propylene/C4+ olefin stream **408** then undergo a second oligomerization **410**. While optional, as illustrated, said streams **406** and **408** are combined into feed stream **438** before the second oligomerization **410** to yield an isoolefinic stream **412**. Further, embodiments may include further processing isoolefinic stream **412** as discussed relative to the further processing of isoolefinic stream **112** including hydroprocessing to produce an isoparaffinic stream.

The process of the first oligomerization **404** may include introducing the ethylene stream **402** into a reactor **442** where an oligomerization reaction of the ethylene stream **402** to an intermediate C4+ olefin stream **444** occurs. Said oligomerization may convert at least 95% of that ethylene in the ethylene stream **402** to C4+ oligomers in one pass through the reactor **442**. A first oligomerization unit may include two or more reactors arranged in series, with the hydrocarbon product from one reactor, including some product oligomers and unreacted ethylene, sent as feed to the next reactor in series to convert additional ethylene to the oligomer product. Alternatively, a first oligomerization unit may include two or more reactors arranged in parallel, for example splitting the feed into two streams to two separate reactors, increase the overall capacity of first oligomerization unit. Further, a hybrid of the foregoing with some reactors arranged in parallel and others in series may be included in a first oligomerization unit.

The intermediate C4+ olefin stream **444** from the reactor **442** is then introduced to a lights removal column **446** to remove components with volatility higher than butenes, and potentially a minor amount of butenes as well, to generate a light fuel gas stream **436**. The higher volatility components in the light fuel gas stream **436** may include mainly methane, ethane, and unreacted ethylene. The separation of saturated hydrocarbons like methane and ethane from the intermediate C4+ olefin stream **444** using the lights removal column **446** may advantageously be less energy intensive and/or require less complicated components than if the saturated hydrocarbons were separated from closer volatility ethylene in the earlier separation **426**. That is, the upstream separation may produce only two streams where the higher volatility components remain present in the ethylene stream. Then, said higher volatility components may be removed at the first oligomerization by inclusion of a lights removal column downstream of the oligomerization reactor. Said lights removal column may be within the first oligomerization unit or downstream thereof.

Another advantage of including a lights removal column downstream of the reactor **442** is that the first oligomerization reaction and first oligomerization catalyst may be largely unaffected by the saturated hydrocarbons, as the saturated hydrocarbons are essentially inert in the first oligomerization reaction. Therefore, the requirements for separating the saturated hydrocarbons in separation **426** can be relaxed or eliminated, which has significant energy use benefits and cost benefits.

FIG. 5 illustrates a nonlimiting example of a method **500** of the present disclosure where a nonlimiting example second oligomerization **510** is described. The disclosure relating to steps, streams, processes, units, etc. with reference numbers with the final two numbers corresponding to a foregoing reference number in FIG. 1, FIG. 2, FIG. 3, and/or FIG. 4 (e.g., propylene/C4+ olefin stream **108**) applies to the corresponding steps, streams, processes, units, etc. having reference numbers with the same final two numbers in FIG. 3 (e.g., propylene/C4+ olefin stream **308**). However, the second oligomerization **510** illustrated in FIG. 5 is a nonlimiting example of a separation and is one of many possible separations that may be used in separations shown in any of the other FIGS. in the present disclosure.

As illustrated, a raw olefin stream **524** enters a separation **526**, which produces an ethylene stream **502**, and a propylene/C4+ olefin stream **508**, and, optionally, a high volatility stream **534** (for example, when the separation **526** occurs according to the separation **326** of FIG. 3). The ethylene stream **502** undergoes a first oligomerization **504** and separation, which produces a C4+ olefin stream **506** and, optionally, a light fuel gas stream **436** (for example, when a lights removal column is used, for example, like the first oligomerization **504** may occur according to the first oligomerization **404** of FIG. 4).

The C4+ olefin stream **506** and the propylene/C4+ olefin stream **508** then undergo a second oligomerization **510**. While optional, as illustrated, said streams **506** and **508** are combined into feed stream **538** before the second oligomerization **510** to yield an isoolefinic stream **512**.

The second oligomerization **510** is illustrated as being conducted in a second oligomerization unit that comprises a reactor **552**, a mogas/distillate fractionation column **556**, and a debutanizer fractionation column **562**.

The feed stream **538** joins with a top recycle stream **568** and a bottom recycle stream **566** to form a combined second oligomerization reactor feed stream **550** comprising C4-C10+ olefins that may contain no greater than about 10

wt % C10+ olefins. Combined feed stream **550** is provided to reactor **552** that generates a reactor product **554** rich in distillate range C10+ olefins (e.g., C10+ isoolefins), along with unreacted and newly made C4-C9 olefins of various isomers.

The reactor product **554** is directed to the mogas/distillate fractionation column **556** that separates a C9- or C10- first mogas stream **558** from a C10+ isoolefin stream **512**. The C10+ isoolefin stream **512** is removed from second oligomerization unit **510** and can be used for a variety of applications. The C9- first mogas stream **558** is split into two streams, typically with the majority becoming the top recycle stream **568** and the rest becoming a debutanizer feed stream **560**. The debutanizer feed stream **560** is sent to a debutanizer fractionation column **562** that separates a C4-purge stream **540** from a C5+ second mogas stream **564**. The C4- purge stream **540** is removed from second oligomerization unit **510** while the C5+ second mogas stream **564** is split into two streams, typically with the majority becoming the bottom recycle stream **566** and the rest becoming a mogas product purge stream **548** that is also removed from second oligomerization unit **510**.

As described above, the propylene/C4+ olefin stream **508** and the C4+ olefin stream **506** may be separately introduced to the reactor **552**. In variations within the scope of the present disclosure, depending on the exact compositions involved, including olefins and potential small concentration contaminants, it may be desirable to provide each of the streams **506** and **508** to separate points within second oligomerization unit. For example, the C4+ olefin stream **508** may contain up to 15 wt % or even greater of C10+ olefins that are already in the distillate range. To minimize the load on reactor **552**, the propylene/C4+ olefin stream **508** can be a feed gas for reactor **552** and the C4+ olefin stream **506** can be added directly to the mogas/distillate fractionation column **556**. In this manner, the mogas/distillate fractionation column **556** will separate the C10+ molecules in the C4+ olefin stream **506** directly into the isoolefin stream **512**, and separate the lower carbon number molecules in the C4+ olefin stream **506** into the mogas range material **558**, the great majority of which will become a recycle feed to the reactor **552** to produce additional isoolefin stream **512**.

Further, embodiments may include further processing isoolefinic stream **512** as discussed relative to the further processing of isoolefinic stream **112** including hydroprocessing to produce an isoparaffinic stream.

Isoparaffinic Blend Component for Blended Jet/Kerosene Boiling Range Products

In various aspects, an isoparaffinic blend component (e.g., all or a portion of an isoparaffinic stream discussed in FIGS. **1-5**) can be used to form blended products that can correspond to jet fuels and/or jet fuel blending components. Optionally, an isoolefinic blend component can be used instead of or in addition to an isoparaffinic blend component.

In this discussion, to be either an isoparaffinic blend component or an isoolefinic blend component, a fraction will contain 50 wt % or more of a combined weight of isoparaffins and iso-olefins, or 60 wt % or more, or 70 wt % or more, or 80 wt % or more, such as up to the fraction substantially being composed of isoparaffins and iso-olefins (i.e., less than 5.0 wt % of other types of hydrocarbons/compounds, or less than 3.0 wt %, or less than 1.0 wt %, such as down to zero). In addition to the above, an isoparaffinic blend component refers to a fraction containing less than 5.0 wt % iso-olefins and 80 wt % or more of isoparaffins (relative to the weight of the fraction), or 85 wt % or more, or 90 wt % or more, such as up to having substantially all

of the fraction correspond to isoparaffins. An isoolefinic blend component refers to a fraction that a) satisfies the requirement for the combined amount of iso-olefins and isoparaffins, and b) contains 5.0 wt % or more of iso-olefins, or 25 wt % or more, or 50 wt % or more, or 70 wt % or more, such as up to having substantially all of the fraction correspond to iso-olefins.

In various aspects, an isoparaffinic blend component and/or an isoolefinic blend component can have one or more of the following properties. In some aspects, 80 wt % or more of the blend component, or 90 wt % or more, or 94 wt % or more, or 97 wt % or more, is composed of C₉ to C₂₀ iso-olefins, isoparaffins, or a combination thereof. In some aspects, 2.0 wt % to 25 wt % of the blend component is composed of C₉ hydrocarbons, or 2.0 wt % to 15 wt %, or 5.0 wt % to 25 wt %, or 5.0 wt % to 15 wt %, or 2.0 wt % to 10 wt %. In some aspects, 1.0 wt % to 15 wt % of the blend component is composed of C₁₇₊ hydrocarbons, or 2.5 wt % to 15 wt %. In some aspects, 1.0 wt % to 15 wt % of the blend component is composed of C₁₇ and/or C₁₈ hydrocarbons, or 2.5 wt % to 15 wt %, or 1.0 wt % to 10 wt %, or 2.5 wt % to 10 wt %. In some aspects, the blend component can contain 5.0 wt % or less of C₁₉₊ hydrocarbons, or 3.0 wt % or less, or 1.0 wt % or less, such as down to having substantially no content of C₁₉₊ hydrocarbons. In some aspects, the blend component can include 5.0 wt % or less of C₈₋ hydrocarbons, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, such as down to 0.1 wt % or possibly still lower (i.e., substantially no C8-content). In some aspects, the blend component has a specific gravity at 15° C. of 0.730 g/cm³ to 0.775 g/cm³.

In some aspects, the blend component can contain 60 wt % to 90 wt % of C₁₁ to C₁₈ isoparaffins, based on the weight of the blend component. Additionally or alternately, the blend component can contain 50 wt % to 75 wt % of C₁₂ to C₁₆ isoparaffins, based on the weight of the blend component. This is particularly advantageous for the flexible use of the composition as an aviation or diesel fuel.

In various aspects, the blend component can contain a reduced or minimized amount of aromatics. This can correspond to containing 5.0 wt % or less of aromatics, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, or 0.1 wt % or less, such as down to having substantially no aromatics content.

In various aspects, the blend component can have a flash point of 38° C. or higher, or 40° C. or higher, or 45° C. or higher, or 50° C. or higher, or 55° C. or higher, such as up to 60° C. or possibly still higher. Additionally or alternately, the blend component, when tested alone (i.e., prior to blending with another fraction), can have a Jet Fuel Thermal Oxidation Test (JFTOT) breakpoint result of 260° C. or higher, or 270° C. or higher, or 280° C. or higher, such as up to 320° C. or possibly still higher.

In some aspects, the blend component, prior to adding any additives, can have an electrical conductivity of 10 pS/m or less (according to ASTM Test Method D2624), such as down to having substantially no electrical conductivity. It is noted that an isoparaffinic blend component as described herein has a good response to conductivity additives. After addition of conventional additives for conductivity, an isoparaffinic blend component can have a conductivity of 50 pS/m to 600 pS/m.

An isoparaffinic blend component can be blended with one or more other fractions to form a kerosene/jet boiling range product. Examples of fractions that can be blended with an isoparaffinic blend component include, but are not limited to, conventional jet fractions, mineral naphtha and/or

jet and/or diesel boiling range fractions, and various types of synthetic naphtha, jet, and/or diesel boiling range fractions, such as sustainable aviation fuel fractions and/or Fischer-Tropsch fractions. Other challenged fractions where at least a portion of the fraction corresponds to jet/kerosene boiling range components can also be blended with an isoparaffinic blend component.

In various aspects, a blended product can contain 1.0 vol % or more of an isoparaffinic blend component, or 10 vol % or more, or 30 vol % or more, or 50 vol % or more, or 65 vol % or more, or 75 vol % or more, such as up to 99 vol % or possibly still higher. In some aspects, such a blended product can include 1.0 vol % to 20 vol % of an isoparaffinic blend component, or 1.0 vol % to 15 vol %, or 5.0 vol % to 20 vol %, or 5.0 vol % to 15 vol %, or 10 vol % to 20 vol %.

In other aspects, such a blended component can include 30 vol % to 99 vol % of an isoparaffinic blend component, or 30 vol % to 95 vol %, or 30 vol % to 80 vol %, or 30 vol % to 60 vol %, or 30 vol % to 45 vol %, or 50 vol % to 99 vol %, or 50 vol % to 95 vol %, or 50 vol % to 80 vol %, or 70 vol % to 99 vol %.

In some aspects, 0.1 wt % to 15 wt % of the resulting blended product can be C₁₇₊ hydrocarbons, or 1.0 wt % to 15 wt %, or 2.5 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 1.0 wt % to 10 wt %, or 2.5 wt % to 10 wt %, or 1.0 wt % to 6.0 wt %, or 2.5 wt % to 6.0 wt %, or 1.0 wt % to 3.0 wt %, or 0.1 wt % to 6.0 wt %, or 0.1 wt % to 3.0 wt %.

In some aspects, 0.1 wt % to 15 wt % of the resulting blended product can be C₁₇ and/or C₁₈ hydrocarbons. For example, the resulting blended product can include 0.1 wt % or more of C₁₇-C₁₈ hydrocarbons, or 1.0 wt % or more, or 1.5 wt % or more, or 2.0 wt % or more, or 4.0 wt % or more, or 6.0 wt % or more, or 10 wt % or more, such as up to 15 wt %.

In some aspects, the resulting blended product can contain 5.0 wt % or less of C₁₉₊ hydrocarbons, or 3.0 wt % or less, or 1.0 wt % or less, or 0.1 wt % or less, such as down to having substantially no content of C₁₉₊ hydrocarbons.

In some aspects, the resulting blended product can have an unexpectedly high content of C₉ hydrocarbons. In such aspects, the resulting blended product can contain 5.0 wt % or more of C₉ hydrocarbons, or 10 wt % or more, or 15 wt % or more, such as up to 25 wt % or possibly still higher.

In various aspects, the resulting blended product can have a specific gravity at 15° C. of 0.775 g/cm³ to 0.840 g/cm³. Additionally or alternately, the resulting blended product can have a flash point of 38° C. or higher, or 40° C. or higher, or 45° C. or higher, or 50° C. or higher, such as up to 60° C. or possibly still higher. Further additionally or alternately, the resulting blended product can have a Jet Fuel Thermal Oxidation Test (JFTOT) breakpoint result of 260° C. or higher, or 270° C. or higher, or 280° C. or higher, such as up to 320° C. or possibly still higher. Still further additionally or alternately, the resulting blended product can have a freeze point of -40° C. or less, or -47° C. or less, or -50° C. or less, or -55° C. or less, such as down to -70° C. or possibly still lower.

In some aspects, the resulting blended product can have a final boiling point of 300° C. or less, even though the resulting blended product contains 1.0 wt % or more of C₁₇₊ hydrocarbons.

In various aspects, the resulting blended product can contain a reduced or minimized amount of aromatics. This can correspond to containing 15 wt % or less of aromatics, or 10 wt % or less, or 5.0 wt % or less, or 3.0 wt % or less, or 1.0 wt % or less, or 0.5 wt % or less, or 0.1 wt % or less, such as down to having substantially no aromatics content. Additionally or alternately, the sulfur content can be 500

wppm or less, or 250 wppm or less, or 100 wppm or less, or 10 wppm or less, such as down to 0.5 wppm or possibly still lower.

In some aspects, the resulting blended product can include at least a portion of one or more conventional jet fuel(s). A conventional jet fuel is defined herein as a fraction that already qualifies as a jet fuel under at least one of ASTM D1655, UK Ministry of Defence Standard 91-091, and Canadian General Standards Board 3.23. In such aspects, the resulting blended product can include 1.0 vol % to 99 vol % of a conventional jet fuel fraction, or 1.0 vol % to 90 vol %, or 1.0 vol % to 70 vol %, or 1.0 vol % to 50 vol %, or 1.0 vol % to 30 vol %, or 1.0 vol % to 10 vol %, or 10 vol % to 70 vol %, or 10 vol % to 50 vol %, or 10 vol % to 30 vol %, or 30 vol % to 70 vol %.

Thus, the resulting blended product can, in some aspects, include 50 vol % or less of a conventional jet fuel fraction, or 30 vol % or less, or 10 vol % or less, such as down to 1.0 vol % or possibly still lower.

In some aspects, the resulting blended product can include at least a portion of one or more mineral kerosene/jet boiling range fraction(s). In such aspects, the resulting blended product can include 1.0 vol % to 99 vol % of a jet/kerosene boiling range fraction, or 1.0 vol % to 90 vol %, or 1.0 vol % to 70 vol %, or 1.0 vol % to 50 vol %, or 1.0 vol % to 30 vol %, or 1.0 vol % to 10 vol %, or 10 vol % to 70 vol %, or 10 vol % to 50 vol %, or 10 vol % to 30 vol %, or 30 vol % to 70 vol %.

Thus, the resulting blended product can, in some aspects, include 50 vol % or less of a jet/kerosene boiling range fraction, or 30 vol % or less, or 10 vol % or less, such as down to 1.0 vol % or possibly still lower.

In some aspects, the resulting blended product can include at least a portion of one or more synthetic jet boiling range fraction(s), optionally as defined in ASTM D7566. In such aspects, the resulting blended product can include 1.0 vol % to 99 vol % of a synthetic jet boiling range fraction, or 1.0 vol % to 90 vol %, or 1.0 vol % to 70 vol %, or 1.0 vol % to 50 vol %, or 1.0 vol % to 30 vol %, or 1.0 vol % to 10 vol %, or 10 vol % to 70 vol %, or 10 vol % to 50 vol %, or 10 vol % to 30 vol %, or 30 vol % to 70 vol %.

Thus, the resulting blended product can, in some aspects, include 50 vol % or less of a synthetic jet boiling range fraction, or 30 vol % or less, or 10 vol % or less, such as down to 1.0 vol % or possibly still lower.

It is noted that an isoparaffinic and/or component can be blended with a plurality of different types of fractions. For example, in some aspects, a blended product can include two or more (or three or more) of a conventional jet fuel fraction, a mineral jet boiling range fraction, and a synthetic fraction. Examples of synthetic fractions include bio-derived fractions, sustainable aviation fuels, and/or a Fischer-Tropsch fractions.

In some aspects, after blending components together to form a kerosene/jet fuel boiling range fraction, it may be desirable to further treat the kerosene/jet boiling range fraction for any convenient reason. Examples of further treatment methods can include, but are not limited to, wet treating, clay treatment, acid and/or caustic treatment, mercaptan oxidation, salt drying, and hydroprocessing.

Distribution of Carbon Atom Types in Isoparaffinic Stream and Related Blend Components and Blends

In some aspects, an isoparaffinic stream formed according to this method may have a distribution of types of carbon atoms within the hydrocarbons of the isoparaffinic stream that is distinct from a fraction containing isoparaffins that are formed by another method, such as by isomerization of an n-paraffin feed. This difference in the types of carbon atoms

can be characterized using various types nuclear magnetic resonance (NMR) analysis, including ^1H NMR and ^{13}C NMR.

^1H NMR can be used to roughly characterize the amount of hydrogen in a sample that corresponds to CH_3 groups (primary or terminal carbons), CH_2 groups (secondary carbons) and CH groups (tertiary carbons). The reason that this is only an approximate characterization is that the presence of aromatic rings can alter the resonance location for certain types of hydrogens. However, this impact of aromatic rings is general for all types of ^1H NMR, and the change in the detected number of CH_3 groups, CH_2 groups, and CH groups is minimal for any sample containing less than 60 wt % aromatics. Thus, ^1H NMR can be used to characterize in a repeatable manner the content of CH_3 groups, CH_2 groups, and CH groups in a sample.

In general, ^1H NMR can be used to characterize the number of CH_3 groups, CH_2 groups, and CH groups in a sample in the following manner. Based on peak position, ^1H NMR can generally characterize hydrogens in a hydrocarbon (or hydrocarbon-like) sample as falling into one of 6 types of groups: 1) hydrogens attached to an aromatic ring; 2) hydrogens attached to carbons that are part of an olefinic bond; 3) hydrogens attached to a carbon that is alpha to an aromatic ring (i.e., hydrogen is attached to a first carbon, the first carbon is attached to a second carbon that is part of an aromatic ring); 4) hydrogens that are part of a CH_3 ; 5) hydrogens that are part of a CH_2 group, and 6) hydrogens that are part of a CH group. The peaks corresponding to these 6 types of hydrogen can then be integrated. This provides relative ratios of for the amount of each type of hydrogen that is present. These ratios can then be used to determine the relative percentages of the corresponding types of carbons that are present in a sample. In particular, for the hydrogens attached to CH_3 groups and CH_2 groups, the amount of hydrogens present needs to be divided by 3 or 2, respectively, in order to convert the relative hydrogen amount detected by NMR into a relative number of CH_3 groups or CH_2 groups.

In this discussion, " CH_3 groups" are defined as paraffinic/aliphatic CH_3 groups as determined based on ^1H NMR. This is determined by integration of the hydrogen peak corresponding to the peak in the NMR spectrum that corresponds to hydrogens that are part of a CH_3 group. It is noted that hydrogens from any CH_3 group where the carbon of the CH_3 group is in the alpha or beta position relative to an aromatic ring (e.g., the CH_3 is part of a methyl or ethyl group attached to an aromatic ring) are not part of this peak. CH_3 groups in a side chain from an aromatic ring that are in the gamma position or farther away are included here. Therefore, to the degree aromatics are present, the amount of CH_3 groups detected based on ^1H NMR may be slightly lower than the actual content of CH_3 groups. However, this is a small error for samples having less than 60 wt % aromatics. Thus, in this discussion, references to CH_3 groups in a sample are defined as CH_3 groups as detected by ^1H NMR, without an attempt to correct the NMR value based on this possible undercounting error due to the presence of aromatics.

In this discussion, " CH_2 groups" are defined as paraffinic/aliphatic CH_2 groups as determined based on ^1H NMR. This is determined by integration of the hydrogen peak corresponding to the peak in the NMR spectrum that corresponds to hydrogens that are part of a CH_2 group. It is noted that hydrogens from any CH_2 group that is alpha or beta to an aromatic ring are not part of this peak. Additionally, hydrogens from a CH_3 group that is beta to an aromatic ring are included in this peak. Therefore, to the degree aromatics are

present, the amount of CH_2 groups detected based on ^1H NMR may be slightly lower, slightly higher, or the same as the actual content of CH_2 groups. However, this is a small error for samples having less than 60 wt % aromatics. Thus, in this discussion, references to CH_2 groups in a sample are defined as CH_2 groups as detected by ^1H NMR, without an attempt to correct the NMR value based on possible undercounting and/or overcounting errors due to the presence of aromatics. It is noted that CH_2 groups that are part of a naphthene ring are included in the CH_2 NMR peak.

In this discussion, " CH groups" are defined as paraffinic/aliphatic CH groups as determined based on ^1H NMR. This is determined by integration of the hydrogen peak corresponding to the peak in the NMR spectrum that corresponds to hydrogens that are part of a CH group. As noted above, any hydrogens directly attached to an aromatic ring are not included in this peak. Additionally, it is noted that hydrogens from any CH group that is alpha or beta to an aromatic ring are not part of this peak. Further, hydrogens from a CH_2 group that is beta to an aromatic ring are included in this peak. Therefore, to the degree aromatics are present, the amount of CH groups detected based on ^1H NMR may be slightly lower, slightly higher, or the same as the actual content of CH groups. However, this is a small error for samples having less than 60 wt % aromatics. Thus, in this discussion, references to CH groups in a sample are defined as paraffinic/aliphatic CH groups as detected by ^1H NMR, without an attempt to correct the NMR value based on possible undercounting and/or overcounting errors due to the presence of aromatics. It is noted that CH groups that are part of a naphthene ring are included in the CH NMR peak.

In various aspects, an isoparaffinic stream (e.g., an isoparaffinic stream discussed in FIGS. 1-5) can have a ratio of CH_3 groups (as determined based on ^1H NMR) to CH_2 groups (as determined based on ^1H NMR) of 1.01 to 1.35, or 1.01 to 1.25, or 1.10 to 1.35, or 1.10 to 1.25. By blending an at least a portion of the isoparaffinic stream (also referred to as an isoparaffinic blend component) with another fraction, a resulting blend can be formed that has a ratio of CH_3 groups to CH_2 groups (both as determined based on ^1H NMR) of 1.01 to 2.30, or 1.01 to 2.00, or 1.01 to 1.80, or 1.01 to 1.50, or 1.01 to 1.15, or 1.36 to 2.30, or 1.36 to 2.00, or 1.36 to 1.80, or 1.70 to 2.30. It is noted that the ratio of CH_3 to CH_2 groups can vary depending on the type of fraction that is blended with an isoparaffinic blend component. For example, blending an isoparaffinic blend component with a mineral jet boiling range fraction, a mineral distillate boiling range fraction, or a Fischer-Tropsch fraction and/or fraction with a high n-paraffin content, will tend to result in blends having a lower ratio. By contrast, blending an isoparaffinic blend component with a fraction that has been highly isomerized in a catalytic dewaxing/isomerization process will tend to result in blends having a higher ratio.

In addition to characterizing hydrogen for full samples, ^{13}C NMR was used to characterize the quaternary carbon content of the C_{12} fraction of various samples. For this type of measurement, gas chromatography can be used to separate the C_u compounds present in a sample from the remaining hydrocarbons. A straightforward method that can be used for forming a C_{12} fraction is the normal paraffin (or linear paraffin) gas chromatograph method. That is, for an appropriate gas chromatograph with a separation column of adequate resolution, a normal paraffin of a given carbon number is assumed to delineate a peak, above which, species may be assumed to comprise the carbon number of the next higher carbon number normal paraffin peak. For example, all

peaks for material eluting in between the peaks for n-decane and n-undecane are assumed to be C₁₁ species.

The resulting C₁₂ fraction can then be characterized using ¹³C NMR. It has been discovered that the C₁₂ fraction of an isoparaffinic blend component made according to the methods described herein can have an unexpectedly low content of quaternary carbons relative to a fraction made by catalytic isomerization of n-paraffins. In such aspects, the quaternary carbon content of the C₁₂ fraction of an isoparaffinic blend component can be 1.5% or less of the total carbons present in the C₁₂ fraction, or 1.4% or less, or 1.3% or less, such as down to 1.0% or possibly still lower.

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the present specification and associated claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the incarnations of the present inventions. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claim, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

One or more illustrative incarnations incorporating one or more invention elements are presented herein. Not all features of a physical implementation are described or shown in this application for the sake of clarity. It is understood that in the development of a physical embodiment incorporating one or more elements of the present invention, numerous implementation-specific decisions must be made to achieve the developer's goals, such as compliance with system-related, business-related, government-related and other constraints, which vary by implementation and from time to time. While a developer's efforts might be time-consuming, such efforts would be, nevertheless, a routine undertaking for those of ordinary skill in the art and having benefit of this disclosure.

While compositions and methods are described herein in terms of "comprising" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps.

ADDITIONAL EMBODIMENTS

Embodiment 1. A method for producing a blended jet boiling range composition stream comprising: oligomerizing an ethylene stream to a C₄₊ olefin stream in a first olefin oligomerization unit comprising a serial reactor and a lights removal column, wherein the C₄₊ olefin stream contains no greater than 10 wt % of methane, ethylene, and ethane combined; wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen; oligomerizing the C₄₊ olefin stream and a propylene/C₄₊ olefin stream in a second oligomerization unit to produce an isoolefinic stream; subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as treat gas to produce an isoparaffinic stream having no greater than 10 wt % olefin content; and using least a portion of the isoparaffinic stream to create the blended jet boiling range composition comprising: 30 vol % to 99 vol % of an isoparaffinic blend component sourced from the isoparaffinic stream containing 80 wt % or more of isoparaffins, 5.0 wt % or less

of olefins, and 5.0 wt % or less of C₁₉₊ hydrocarbons; 1.0 vol % to 70 vol % of a mineral jet boiling range fraction; and a T₁₀ distillation point of 205° C. or less, a final boiling point of 300° C. or less, a freeze point of -40° C. or lower, and 2.0 wt % or more of C₁₇-C₁₈ hydrocarbons.

Embodiment 2. The method of Embodiment 1, wherein the C₄₊ olefin stream contains no greater than 5 wt % of methane, ethylene, and ethane combined.

Embodiment 3. The method of any one of Embodiments 1-2, wherein the C₄₊ olefin stream contains no greater than 2000 wppm of methane, ethylene, and ethane combined.

Embodiment 4. The method of any one of Embodiments 1-3, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen.

Embodiment 5. The method of any one of Embodiments 1-4, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen.

Embodiment 6. The method of any one of Embodiments 1-5, wherein the C₄₊ olefin stream and the propylene/C₄₊ olefin stream combine before the second oligomerization.

Embodiment 7. The method of any one of Embodiments 1-6, wherein the first oligomerization unit utilizes a homogeneous catalyst, and wherein the second oligomerization unit utilizes a heterogeneous catalyst.

Embodiment 8. The method of any one of Embodiments 1-7, wherein the second oligomerization recycles a portion of the C₄₊ olefin stream that is not oligomerized to pass it through the second oligomerization again.

Embodiment 9. The method of any one of Embodiments 1-8 further comprising: converting a methanol to olefins to produce a raw olefin stream; wherein the raw olefin stream comprises ethylene, propylene and C₄₊ olefins, wherein at least 10 wt % of all olefins in the raw olefin stream are ethylene, and further containing at least 1000 wppm of each methane and ethane, and at least 100 wppm of each carbon monoxide and hydrogen; and separating the raw olefin stream to remove hydrogen, carbon monoxide, propylene and C₄₊ olefins from the raw olefin stream, and produce the ethylene stream.

Embodiment 10. The method of Embodiment 9, wherein the ethylene stream contains at least 90% of the ethane present in the raw olefin stream.

Embodiment 11. The method of Embodiment 9, wherein the methanol is converted to olefins by using a silicoaluminophosphate catalyst, an aluminosilicate catalyst, or steam cracking.

Embodiment 13. A method for producing a blended jet boiling range composition comprising: providing a raw olefin stream comprising ethylene, propylene and C₄₊ olefins, wherein at least 10 wt % of all olefins in the raw olefin stream are ethylene, and further containing at least 1000 wppm of each methane and ethane, and at least 100 wppm of each carbon monoxide and hydrogen; subjecting the raw olefin stream to a separation operation to remove hydrogen, carbon monoxide, propylene and C₄₊ olefins from the raw olefin stream, and produce an ethylene stream containing at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen, wherein at least 95 wt % of all the ethylene in the raw olefin stream is recovered in the ethylene stream; providing at least a portion of the ethylene stream to a first olefin oligomerization unit comprising one or more serial reactors and a lights removal

column, to convert in a single pass through the serial reactor(s) at least 90% of the ethylene contained in the ethylene stream to a second C4+ olefin stream containing no greater than 10 wt % of methane, ethylene, and ethane combined; providing at least a portion of each of the propylene and the C4+ olefins removed from the raw olefins stream, and at least a portion of the second C4+ stream to a second olefin oligomerization unit to produce an isoolefinic stream; and subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as a treat gas to produce an isoparaffinic stream having no greater than 10 wt % olefin content; and using least a portion of the isoparaffinic stream to create the blended jet boiling range composition comprising: 30 vol % to 99 vol % of an isoparaffinic blend component sourced from the isoparaffinic stream containing 80 wt % or more of isoparaffins, 5.0 wt % or less of olefins, and 5.0 wt % or less of C19+ hydrocarbons; 1.0 vol % to 70 vol % of a mineral jet boiling range fraction; and a T10 distillation point of 205° C. or less, a final boiling point of 300° C. or less, a freeze point of -40° C. or lower, and 2.0 wt % or more of C17-C18 hydrocarbons.

Embodiment 14. The method of Embodiment 13, wherein the C4+ olefin stream contains no greater than 5 wt % of methane, ethylene, and ethane combined.

Embodiment 15. The method of any one of Embodiments 13-14, wherein the C4+ olefin stream contains no greater than 2000 wppm of methane, ethylene, and ethane combined.

Embodiment 16. The method of any one of Embodiments 13-15, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen.

Embodiment 17. The method of any one of Embodiments 13-16, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen.

Embodiment 18. The method of any one of Embodiments 13-17, wherein the ethylene stream contains at least 90% of the ethane present in the raw olefin stream.

Embodiment 19. The method of any one of Embodiments 13-18, wherein the separation operation comprises: a deethanizer distillation column that separates propylene and C4+ from the raw olefin stream; and a demethanizer distillation column that separates methane, hydrogen, and carbon monoxide from the raw olefin stream to produce the ethylene stream.

Embodiment 20. The method of Embodiment 19 further comprising: additional distillation columns in the separation operation, wherein the propylene is separated from C4+ olefins and then further separated from propane and components of similar or lower volatility.

Embodiment 21. The method of any one of Embodiments 13-20, wherein the first oligomerization unit utilizes a homogeneous catalyst, and wherein the second oligomerization unit utilize a heterogeneous catalyst.

Embodiment 22. The method of any one of Embodiments 13-21, wherein the second oligomerization unit comprises: a serial reactor; a distillate fractionation column that outputs the isoolefinic stream; and a debutanizer fractionation column that purges C4- olefins.

Embodiment 23. The method of Embodiment 22, wherein the distillate fractionation column also outputs C9- olefins, of which a first portion is recycled to the serial reactor and a second portion is sent to the debutanizer fractionation column.

Embodiment 24. The method of Embodiment 22, wherein the debutanizer fractionation column also outputs C5+ olefins, of which a first portion is recycled to the serial reactor and a second portion is purged.

Embodiment 25. The method of Embodiment 22, wherein the second C4+ stream travels first to the distillate fractionation tower when entering the second oligomerization unit, while the propylene and the C4+ olefins removed from the raw olefins stream travel first to the serial reactor.

Embodiment 26. The method of any one of Embodiments 13-25 further comprising: converting a methanol to olefins to produce a raw olefin stream.

Embodiment 27. The method of Embodiment 26, wherein the methanol is converted to olefins by using a silicoaluminophosphate catalyst, an aluminosilicate catalyst, or steam cracking.

To facilitate a better understanding of the embodiments of the present invention, the following examples of preferred or representative embodiments are given. In no way should the following examples be read to limit, or to define, the scope of the invention.

EXAMPLES

Example 1—Carbon Chain Length Distribution in Isoparaffinic Blend Component

One of the unusual features of the isoparaffinic blend component as described herein is that the isoparaffinic blend component can contain a substantial portion of C₁₇₊ hydrocarbons while still forming a blend with a final boiling point of 300° C. or less, as measured according to ASTM D86. To illustrate this, several different samples of isoparaffinic blend component were formed using the synthesis methods described herein. Table 1 shows the volume percentage of the hydrocarbon chain lengths in the resulting isoparaffinic blend components. The samples are referred to as IPB 1, 2, and 3 (for Isoparaffinic Blend Component). For comparison, the hydrocarbon chain length distribution in a representative JET A-1 sample is also shown.

TABLE 1

Hydrocarbon Chain Length Distribution									
[vol %]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20
JET A-1	1.7	3.2	7.3	12.7	15.2	27.4	13.4	1.5	0.0
IPB 1	0.3	3.8	6.6	12.3	24.3	14.3	10.7	2.9	1.4
IPB 2	0.2	15.1	5.5	10.3	20.1	11.9	8.9	2.4	1.1
IPB 3	0.2	9.6	9.6	10.9	17.4	14.2	9.9	3.3	1.2

As shown in Table 1, the representative JET A-1 sample includes less than 2.0 vol % of C₁₇-C₁₈ components, and no C₁₉ or C₂₀ components. By contrast, each of the isoparaffinic blend components includes more than 3.0 vol % of C₁₇-C₁₈ hydrocarbons, as well as more than 4.5 vol % of C₁₇₊ hydrocarbons.

The increased concentration of C₁₇₊ hydrocarbons in the isoparaffinic blend components can result in a corresponding increase in C₁₇₊ hydrocarbons in blends that include a portion of an isoparaffinic blend component. Tables 2-4 show the volume percentage of hydrocarbons of various chain lengths that would be incorporated into a blended product that included 70 vol % of an isoparaffinic blend component (Table 2), 50 vol % (Table 3), or 30 vol % (Table 4).

TABLE 2

Contribution to Blend at 70 vol %									
[vol %]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20
JET A-1	1.2	2.3	5.1	8.9	10.6	19.2	9.4	1.0	0.0
IPB 1	0.2	2.7	4.7	8.6	17.0	10.0	7.5	2.1	1.0
IPB 2	0.2	10.6	3.9	7.2	14.1	8.3	6.2	1.7	0.8
IPB 3	0.1	6.7	6.7	7.7	12.2	10.0	7.0	2.3	0.9

TABLE 3

Contribution to Blend at 50 vol %									
[vol %]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20
JET A-1	0.8	1.6	3.6	6.3	7.6	13.7	6.7	0.7	0.0
IPB 1	0.1	1.9	3.3	6.2	12.1	7.2	5.4	1.5	0.7
IPB 2	0.1	7.6	2.8	5.1	10.1	5.9	4.5	1.2	0.6
IPB 3	0.1	4.8	4.8	5.5	8.7	7.1	5.0	1.6	0.6

TABLE 4

Contribution to Blend at 30 vol %									
[vol %]	C8	C9	C10	C11	C12	C13/14	C15/16	C17/18	C19/20
JET A-1	0.5	1.0	2.2	3.8	4.5	8.2	4.0	0.4	0.0
IPB 1	0.1	1.1	2.0	3.7	7.3	4.3	3.2	0.9	0.4
IPB 2	0.1	4.5	1.7	3.1	6.0	3.6	2.7	0.7	0.3
IPB 3	0.0	2.9	2.9	3.3	5.2	4.3	3.0	1.0	0.4

As shown in Tables 2-4, blends including 70 vol % of an isoparaffinic blend component can include 1.6 vol % or more of C₁₇-C₁₈ hydrocarbons, or 2.0 vol % or more, such as up to 2.3 vol %. For a 50% blend, the isoparaffinic blend component can contribute 1.2 vol % or more of C₁₇-C₁₈ hydrocarbons, such as up to 1.6 vol %. Based on a typical C₁₇-C₁₈ content in a conventional jet fuel of roughly 1.5 vol %, it is clear that an isoparaffinic blend component as described herein can allow for incorporation of a higher volume percentage of C₁₇-C₁₈ hydrocarbons into a potential blended jet fuel product.

Example 2—Blends with Conventional Jet Fuels

The isoparaffinic blend components corresponding to IPB 1 and IPB 2 in Example 1 were used in combination with conventional jet fuels (JET A-1 or JP-5) to form blended jet boiling range products. Even for blends with 50 vol % or more of an isoparaffinic blend component, or 70 vol % or

more, the resulting blended jet boiling range products still satisfied the specification for the corresponding type of jet fuel.

FIG. 6 shows results from characterization of a conventional JET A-1 sample, a sample of IPB 1, a blend formed from 30 vol % IPB 1 and 70 vol % JET A-1, and a blend formed from 70 vol % IPB 1 and 30 vol % JET A-1. As shown in FIG. 6, IPB 1 alone does not satisfy all of the standard requirements for a JET A-1 jet fuel. However, blending 70 vol % of IPB 1 with 30 vol % of a conventional JET A-1 resulted in a blended product that satisfied all of the JET A-1 requirements shown in FIG. 6, with the exception of electrical conductivity. However, the conductivity of a potential jet fuel product can be readily raised to meet the required standard using conventional additives.

As explained in Example 1, the blend containing 70 vol % IPB 1 included at least 2.0 vol % of C₁₇-C₁₈ hydrocarbons even without considering the contributions from the JET A-1. The blend including 70 vol % IPB 1 also provided a higher JFTOT breakpoint temperature and a higher smoke point. In combination with the generally beneficial cold flow properties of an isoparaffinic blend component, FIG. 6 shows the value of an isoparaffinic blend component as described herein for potentially returning off-specification jet fuel samples back to specification.

A similar characterization was performed on a JET A-1 sample, IPB 2, a blend of 30 vol % IPB 2 with 70 vol % JET A-1, and a blend of 70 vol % IPB 2 with 30 vol % JET A-1. The results from characterization of these blend products are shown in FIG. 7. Similar to FIG. 6, blending of 50 vol % or more, or 70 vol % or more of an isoparaffinic blend component with a conventional jet fuel sample results in a blended product that can still satisfy all of the required standards that are shown in FIG. 7.

Example 3—Isoparaffinic Blend Component as
Lubricity Improver

It has been discovered that in aspects where the resulting blended product includes at least 10 vol % of a mineral jet boiling range fraction and 40 vol % or more (or 50 vol % or more) of an isoparaffinic blend component, the resulting blended product can have an unexpectedly improved lubricity. Lubricity can be measured based on wear scar diameter as determined according to ASTM D5001. For example, such a blended product can include 10 vol %-50 vol % of a mineral jet boiling range fraction, or 10 vol % to 60 vol %, or 20 vol % to 50 vol %, or 20 vol % to 60 vol %. Such a blended component can also include 40 vol % to 90 vol % of an isoparaffinic blend component, or 50 vol % to 90 vol %, or 40 vol % to 80 vol %, or 50 vol % to 80 vol %.

The unexpected nature of the lubricity improvement when adding 50 vol % or more of an isoparaffinic blend component to a mineral jet boiling range fraction can be understood by comparing the lubricity behavior of the blends shown in Table 5. Table 5 shows results from testing various jet boiling range fractions under the method of ASTM D5001 to determine a wear scar diameter. In Table 5, the first two samples correspond to neat samples of JET A-1 and JP-5. The remaining samples are blends of an isoparaffinic blend component (either IPB-1 or IPB-2) with the JET A-1 or JP-5. Conventionally, it would be expected that adding a highly paraffinic blend component to a mineral jet boiling range fraction would result in poorer lubricity performance. For comparison, it is noted that some diesel fuel standards have a maximum wear scar diameter under the ASTM D5001 of 0.85 mm or less.

TABLE 5

Measured Lubricity Values for Jet Boiling Range Fractions		
Fuel	Wear Scar Diameter	Test Method
100% JET A-1	0.72 mm	D5001
100% JP-5	0.62 mm	D5001
30% IPB-1/70% JET A-1	0.67 mm	D5001
70% IPB-1/30% JET A-1	0.52 mm	D5001
30% IPB-2/70% JET A-1	0.68 mm	D5001
70% IPB-2/30% JET A-1	0.53 mm	D5001
25% IPB-1/75% JP-5	0.63 mm	D5001
50% IPB-1/50% JP-5	0.60 mm	D5001

As shown in Table 5, at blend amounts of 30 vol % of either IPB-1 or IPB-2 with JET A-1, if a linear weighted average model is used to describe the wear scar diameter result for the blends, the linear weighted average model predicts that IPB-1 or IPB-2 alone would have a wear scar diameter of roughly 0.60 mm. By contrast, for the blends including 50 wt % or more of IPB-1 or IPB-2, a linear weighted average model predicts a wear scar diameter below 0.60 mm. It is further noted that for blends of higher amounts of an isoparaffinic blend component with the JET A-1 sample (such as 50 vol % or more of an isoparaffinic blend component), the wear scar diameter for the blended composition is reduced by 10% or more relative to the wear scar diameter for the mineral jet boiling range fraction alone.

Similarly, for the blend of 25 vol % IPB-1 with JP-5, a linear weighted average model predicts that IPB-1 would have a wear scar diameter of around 0.63 mm. In fact, addition of IPB-1 appears to increase the wear scar diameter when mixed with JP-5, in accordance with the conventional expectation. However, increasing the amount of IPB-1 in

this blend to 50 wt % results in a reduction of wear scar diameter relative to neat JP-5, with a predicted wear scar diameter for neat IPB-1 of roughly 0.58 mm.

Based on Table 5, a synergy is observed for blends at 50% of an isoparaffinic blend component or greater, where an unexpected reduction in wear scar diameter is achieved at larger quantities of isoparaffinic blend component in a blend.

Example 4—¹H NMR Analysis of Blend
Components

The isoparaffinic blend component IPB-1 was formed according to the method described herein, where an isoolefinic blend component was formed by olefin oligomerization. A portion of the isoolefinic blend component was then exposed to hydrotreating conditions to saturate the portion, thus forming the IPB-1 sample. In addition to forming the isoparaffinic blend component, two additional portions of the isoolefinic blend component were exposed to conditions for partial saturation of olefins, resulting in components containing roughly 30 wt % olefins/70 wt % paraffins and 70 wt % olefins/30 wt % paraffins.

The isoolefinic blend component, the isoparaffinic blend component, and the two partially saturated components were characterized using ¹H NMR to characterize the ratio of CH₃ groups to CH₂ groups, as determined from the ¹H NMR results. FIG. 8 shows results from the ¹H NMR analysis. In FIG. 8, the first column of data corresponds to data for the substantially fully saturated isoparaffinic blend component (IPB-1). The second column and third column show the partially saturated products, while the final column corresponds to data for the isoolefinic blend component, as made from the oligomerization process.

As shown in FIG. 8, the isoolefinic blend component (prior to any saturation) had the highest ratio of CH₃ groups to CH₂ groups. As saturation increased, the ratio of CH₃ groups to CH₂ groups was decreased, with the isoparaffinic blend component (IPB-1) having a ratio of CH₃ to CH₂ groups (as determined based on ¹H NMR) of 1.18.

For comparison with the values shown in FIG. 8, a variety of other types of fractions were also characterized using ¹H NMR to determine the ratio of CH₃ groups to CH₂ groups. Table 6 shows the values that were obtained for these various other types of fractions. Where a range is given, this indicates that multiple different samples were characterized, with the range corresponding to the minimum and maximum values.

TABLE 6

CH ₃ /CH ₂ Ratio as Determined by ¹ H NMR for Other Components	
Sample Type	CH ₃ to CH ₂ Ratio
JET A-1	0.75
Diesel	0.57-1.00
Gas Oil	0.54
Primarily Isoparaffin Liquid (formed by catalytic isomerization)	2.50-3.21
Primarily N-Paraffin Liquid	0.24-0.33
Naphthenic Liquid (Petroleum Distillate)	2.35
Fischer-Tropsch Liquid	0.37

As shown in Table 6, liquids with high n-paraffin contents tend to have ratios of CH₃ to CH₂ that are well below 1.00. Commercial fuel products generally have ratios below 1.00, although a high isoparaffin content/low aromatic content

diesel can approach 1.00. Fluids containing high contents of naphthenes have CH_3 to CH_2 ratios above 2.30. Similarly, fractions with high isoparaffin content, where the isoparaffin content is formed by catalytic isomerization, have CH_3 to CH_2 ratios above 2.30.

Example 5—Quaternary Carbon Content

A sample of IPB-1 was separated using a gas chromatograph to form a C_{12} fraction. The resulting C_{12} fraction was analyzed using ^{13}C NMR to determine the content of quaternary carbons in the sample. For comparison, Cu fractions were also formed from two other mineral sources after exposing the sources to deep catalytic isomerization. Table 7 shows the results from analysis of the C_{12} fractions.

TABLE 7

^{13}C NMR Analysis of C_{12} Fractions			
	C_{12} Comparative #1	C_{12} Comparative #2	C_{12} from IPB-1
Average Carbon Number (by GC)	11.95	11.88	12.0
Naphthenic Content	8	8	0
Number of Branches per Molecule	2.97	2.39	2.78
Quaternaries (% of total number of carbons)	1.64	1.77	1.35

As shown in Table 7, the quaternary carbon content of the C_{12} fraction was substantially lower than the other fractions. For both comparative samples, the C_{12} fraction had a quaternary carbon content of greater than 1.60% relative to the total number of carbons in the sample, while the C_{12} fraction from the isoparaffinic blend component has a quaternary carbon content of 1.60% or less, or 1.50% or less, or 1.40% or less, such as down to 1.20% or possibly still lower.

Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular examples and configurations disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative examples disclosed above may be altered, combined, or modified and all such variations are considered within the scope and spirit of the present invention. The invention illustratively disclosed herein suitably may be practiced in the absence of any element that is not specifically disclosed herein and/or any optional element disclosed herein. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise

explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

What is claimed is:

1. A method for producing a blended jet boiling range composition stream comprising:

oligomerizing an ethylene stream to a C_{4+} olefin stream in a first olefin oligomerization unit comprising a serial reactor and a lights removal column, wherein the C_{4+} olefin stream contains no greater than 10 wt % of methane, ethylene, and ethane combined;

wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen;

oligomerizing the C_{4+} olefin stream and a propylene/ C_{4+} olefin stream in a second oligomerization unit to produce an isoolefinic stream;

subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as treat gas to produce an isoparaffinic stream having no greater than 10 wt % olefin content; and

using at least a portion of the isoparaffinic stream to create the blended jet boiling range composition comprising: 30 vol % to 99 vol % of an isoparaffinic blend component sourced from the isoparaffinic stream containing 80 wt % or more of isoparaffins, 5.0 wt % or less of olefins, and 5.0 wt % or less of C_{19+} hydrocarbons;

1.0 vol % to 70 vol % of a mineral jet boiling range fraction; and

a T10 distillation point of 205° C. or less, a final boiling point of 300° C. or less, a freeze point of -40° C. or lower, and 2.0 wt % or more of C_{17} - C_{18} hydrocarbons.

2. The method of claim 1, wherein the C_{4+} olefin stream contains no greater than 5 wt % of methane, ethylene, and ethane combined.

3. The method of claim 1, wherein the C_{4+} olefin stream contains no greater than 2000 wppm of methane, ethylene, and ethane combined.

4. The method of claim 1, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen.

5. The method of claim 1, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen.

6. The method of claim 1, wherein the C_{4+} olefin stream and the propylene/ C_{4+} olefin stream combine before the second oligomerization.

7. The method of claim 1, wherein the first oligomerization unit utilizes a homogeneous catalyst, and wherein the second oligomerization unit utilizes a heterogeneous catalyst.

8. The method of claim 1, wherein the second oligomerization recycles a portion of the C_{4+} olefin stream that is not oligomerized to pass it through the second oligomerization again.

9. The method of claim 1 further comprising:

converting a methanol to olefins to produce a raw olefin stream;

wherein the raw olefin stream comprises ethylene, propylene and C_{4+} olefins, wherein at least 10 wt % of all olefins in the raw olefin stream are ethylene, and further

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containing at least 1000 wppm of each methane and ethane, and at least 100 wppm of each carbon monoxide and hydrogen; and

separating the raw olefin stream to remove hydrogen, carbon monoxide, propylene and C₄₊ olefins from the raw olefin stream, and produce the ethylene stream.

10. The method of claim 9, wherein the ethylene stream contains at least 90% of the ethane present in the raw olefin stream.

11. The method of claim 9, wherein the methanol is converted to olefins by using a silicoaluminophosphate catalyst, an aluminosilicate catalyst, or steam cracking.

12. A method for producing a blended jet boiling range composition comprising:

providing a raw olefin stream comprising ethylene, propylene and C₄₊ olefins, wherein at least 10 wt % of all olefins in the raw olefin stream are ethylene, and further containing at least 1000 wppm of each methane and ethane, and at least 100 wppm of each carbon monoxide and hydrogen;

subjecting the raw olefin stream to a separation operation to remove hydrogen, carbon monoxide, propylene and C₄₊ olefins from the raw olefin stream, and produce an ethylene stream containing at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 20 wppm each of carbon monoxide and hydrogen, wherein at least 95 wt % of all the ethylene in the raw olefin stream is recovered in the ethylene stream;

providing at least a portion of the ethylene stream to a first olefin oligomerization unit comprising one or more serial reactors and a lights removal column, to convert in a single pass through the serial reactor(s) at least 90% of the ethylene contained in the ethylene stream to a second C₄₊ olefin stream containing no greater than 10 wt % of methane, ethylene, and ethane combined; providing at least a portion of each of the propylene and the C₄₊ olefins removed from the raw olefins stream, and at least a portion of the second C₄₊ stream to a second olefin oligomerization unit to produce an isoolefinic stream; and

subjecting at least a portion of the isoolefinic stream to a hydroprocessing process with hydrogen as treat gas to

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produce an isoparaffinic stream having no greater than 10 wt % olefin content; and

using at least a portion of the isoparaffinic stream to create the blended jet boiling range composition comprising:

30 vol % to 99 vol % of an isoparaffinic blend component sourced from the isoparaffinic stream containing 80 wt % or more of isoparaffins, 5.0 wt % or less of olefins, and 5.0 wt % or less of C₁₉₊ hydrocarbons;

1.0 vol % to 70 vol % of a mineral jet boiling range fraction; and

a T10 distillation point of 205° C. or less, a final boiling point of 300° C. or less, a freeze point of -40° C. or lower, and 2.0 wt % or more of C₁₇-C₁₈ hydrocarbons.

13. The method of claim 12, wherein the C₄₊ olefin stream contains no greater than 5 wt % of methane, ethylene, and ethane combined.

14. The method of claim 12, wherein the C₄₊ olefin stream contains no greater than 2000 wppm of methane, ethylene, and ethane combined.

15. The method of claim 12, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 5 wppm each of carbon monoxide and hydrogen.

16. The method of claim 12, wherein the ethylene stream contains at least 50 wt % ethylene, at least 2000 wppm ethane, no greater than 1000 wppm of methane, and no greater than 1 wppm each of carbon monoxide and hydrogen.

17. The method of claim 12, wherein the ethylene stream contains at least 90% of the ethane present in the raw olefin stream.

18. The method of claim 12, wherein the separation operation comprises:

a demethanizer distillation column that separates propylene and C₄₊ from the raw olefin stream; and

a demethanizer distillation column that separates methane, hydrogen, and carbon monoxide from the raw olefin stream to produce the ethylene stream.

19. The method of claim 12, wherein the first oligomerization unit utilizes a homogeneous catalyst, and wherein the second oligomerization unit utilizes a heterogeneous catalyst.

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